SKB TECHNICAL REPORT 93-05

Studies of natural analogues and geological systems. Their importance to performance assessment.

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April 1993

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STUDIES OF NATURAL ANALOGUES AND GEOLOGICAL SYSTEMS. THEIR IMPORTANCE TO PERFORMANCE ASSESSMENT

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Information on SKB technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77), 1984 (TR 85-01), 1985 (TR 85-20), 1986 (TR 86-31), 1987 (TR 87-33), 1988 (TR 88-32), 1989 (TR 89-40), 1990 (TR 90-46), 1991 (TR 91-64) and 1992 (TR 92-46) is available through SKB.

Förord

I denna rapport presenteras en genomgång av studier av naturliga analogier och naturliga geologiska system med avsikten att identifiera och kvantifiera processer och företeelser som är av vikt för funktionen och säkerheten av slutförvar för radioaktivt avfall. De företeelser och processer som studeras omfattar allmänna geokemiska frågeställningar kopplade till funktionen hos när- och fjärrzonen, funktion och teknisk livslängd för konstruktionsmaterial och effekterna av nedisningar. För vart och ett av dessa områden har ett antal väsentliga processer beskrivits. Indikationer på att de förekommer i naturen såväl som kvantitativa bestämningar av parametrar i de modeller som beskriver processerna har samlats in från studier av naturliga analogier och från platsundersökningar. Genomgången har syftat att täcka ett relativt brett fält av frågeställningar på bekostnad av analysens djup. De kvantitativa data som presenteras är huvudsakligen sammanställda från litteraturen. I några få fall har utvärderingar gjorts inom denna studie.

Resultatet av genomgången visar att studier av naturliga analogier och naturliga geologiska system har givit upphov till väsentlig information rörande många frågor som är betydelsefulla för ett slutförvars funktion. I flera fall har resultaten från studier av naturliga analogier visat att processer som antas försiggå i ett sluförvar också kan observeras i naturliga system under förhållanden som liknar de som förutsägs råda i ett framtida slutförvar. Ett exempel på en sådan process är medfällning av klyvningsprodukter och järnoxihydroxider som en analogi för korrosionsprodukter från en stålkapsel. Vidare visar studier av koncentrationsgradienter av uran och andra spårämnen i berget som omger grundvattenledande sprickor att matrisdiffusion försiggår i naturen och att de diffusiviteter som mäts i laboratorier överensstämmer med observationer i naturen. Observationer av kolloider av uran, torium och sällsynta jordartsmetaller i samband med studier av naturliga analogier antyder att kolloiderna inte transporterar väsentliga mängder av dessa spårämnen. Förklaringen kan antingen vara att spårämnena sorberas reversibelt på kolloiderna eller att kolloidernas rörlighet är mycket låg på grund av filtrering eller andra fenomen.

Observationer av naturliga system och arkeologiska fynd har använts för att demonstrera den tekniska livslängden hos de konstruktionsmaterial som bygger upp flerbarriärssystemet i närzonen. Studier av koppar, stål, bentonit, såväl som av olika typer av cement och betong stöder starkt trovärdigheten av förutsägelser om dessa materials långtidsstabilitet under slutförvarsförhållanden.

Naturliga analogier börjar i ökande grad ge tillfälle till testning av termodynamiska löslighets- och specieringsmodeller tillsammans med de termodynamiska databaser som används i funktionsanalyser. Även om detta har genomförts med viss framgång behövs experimentella bestämningar av specieringen in situ för att klara ut en del av de osäkerheter som finns rörande termodynamiska data för vissa grundämnen.

Allmänt sett börjar naturliga analogier nu få ett ökande inflytande på funktionsanalyser för slutförvar. Detta gäller särskilt för processer som pågår under tider är jämförbara med slutförvarets livslängd.

Abstract

This review has involved studies of natural analogues and natural geological systems leading to the identification and quantification of processes and features of importance to the performance and safety of repositories for radioactive waste. The features and processes selected for the study comprise general geochemical issues related to the performance of the near- and the far-field, the performance and durability of construction materials and the effects of glaciation. For each of these areas a number of potentially important processes for repository performance have been described, and evidence for their existence, as well as quantification of parameters of models describing the processes, have been sought from major natural analogue studies and site investigations. The review has aimed at covering a relatively broad range of issues at the expense of in-depth analysis. The quantitative data presented are in most cases compilations of data from the literature; in a few cases results of evaluations made within the current project are included.

The results of the study show that studies of natural analogues and natural geological systems have provided significant information regarding many issues of importance to repository performance. In several cases the evidence from natural analogues has demonstrated that processes assumed to take place in repositories actually occur in natural systems or under conditions similar to those predicted to prevail in a future repository. One example of such a process is coprecipitation of fission products and ferric oxyhydroxides as an analogue to corrosion products from a steel canister. In addition, the study of concentration gradients of uranium and other trace substances in the rock surrounding groundwater conduits confirm that matrix diffusion occurs in nature and that the diffusivities in the rock matrix measured in the laboratory are consistent with the observations in nature. Furthermore, observations within natural analogue studies of colloids associated with uranium, thorium and rare-earth elements indicate that colloids do not appear to transport significant amounts of these trace elements. This would suggest that either the sorption of the trace elements onto the colloids is reversible or the mobility of the colloids is low due to filtration effects or other phenomena.

Observations from natural systems and archaeological artefacts have been used to demonstrate the durability of the different materials comprising the near-field multibarrier system. Studies of copper and steel, bentonite and various types of cement and concrete strongly support the credibility of predicting long-term stability of these materials under repository conditions.

Increasingly, natural analogue studies are providing the opportunity to test the thermodynamic solubility and speciation codes and associated data bases used in performance assessment. This has been carried out with some success. However, in situ speciation measurements are necessary to rectify the large uncertainties which still exist for some elements in the data bases.

In general, natural analogue studies are progressively making their impact felt on repository performance assessment, in particular studying processes which have been occurring over time scales compatible with those predicted for long-term radioactive waste disposal.

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1. Introduction

Studies of natural analogues and geological systems are increasingly being recommended as an essential approach contributing to repository design and performance. The performance assessment (PA) of a high-level radioactive waste repository system involves the use of various scenarios to study the sequence of events that are expected to influence the system over a long period of time. These scenarios are described by different dynamic models that are based on chosen parameters best considered to quantify the character of the system. Models are usually an oversimplification of the system, and are therefore progressively modified to become more realistic and representative of the scenario being described. This is achieved by verification and validation using a continuously up-dated quantitative data base derived not only from laboratory experiments, but increasingly from the study of natural analogues and geological systems. Some schools of opinion consider that such natural systems provide the best known method of testing the long-term safety functions of a high-level radioactive waste repository. Some analogues will be directly comparable to processes predicted to occur in and around the repository, irrespective of environmental differences, whilst others may be only of marginal value in performance assessment due to the overwhelming influence of environmental parameters.

The term 'analogue' is usually loosely defined, referring to both natural and man-made materials. Natural analogues have been defined: 'as the occurrence, in the natural environment, of materials or processes which are the same, or can be related to, those which are predicted to occur in some part of a disposal system, which includes the repository, the surrounding rock formations, and the biosphere' *[IAEA, 1987]*. The essential feature is that they are phenomena which are not controlled by man and, as such, include archaeological evidence.

National analogues and their rational through reasoning by analogy has been addressed by *[Petit, 1992]*. He also pointed out that there is not yet a full consensus of scientific opinion on the actual usefulness of analogue studies. A recent appraisal *[Chapman et al., 1992]* emphasised analogues as pertaining to the chemical and physical perturbations resulting from the impact of an engineered repository facility on the natural geological environment. Such perturbations are assessed by iteratively comparing two sets of systems: a) the engineered system, whereby construction materials are essential components, and b) the natural geological system which may also include anthropogenic artifacts or the consequences of human activities. This definition may be extended, as in this report, to include issues relating to the perturbation of the engineered system by disruptive processes of the natural environment, such as faulting, seismic effects and glaciation.

In addition to the obvious scientific value of natural analogue studies, they also play an increasingly important public relations role. There are clear indications from the informed scientific and technological communities, in addition to the less informed public, that confidence in the reliability of a certain feature or process increases when presented with evidence from natural geological systems. Consequently, reference to natural analogue studies and the resulting data are often used as information material to the media. The dependability of analogues in building confidence is based on the fact that they have developed over time scales comparable to the predicted duration of a repository system. Furthermore, since they have not been influenced or controlled by man, unexpected events and processes can be identified and observed.

References to natural analogues have been made in all safety performance assessments made by SKB, such as KBS-1 on vitrified waste, KBS-2, KBS-3 and SKB-91 on spent fuel, the final safety report (FSR) for the low- and intermediate-level waste repository (SFR), and a supplement to the FSR report which is in fact an additional safety assessment. Natural analogue applications have been mostly concerned with the near-field environment, e.g. the stability of the copper canister and the bentonite overpack. These and other applications are documented in the literature and a summary is given by *[Smellie, 1989]*. Other notable applications have centred around the Swiss radioactive waste programme, e.g. *[Alexander and McKinley, 1992; McKinley and Alexander, 1992; McKinley et al., 1992; Pate et al., 1992]*.

These earlier examples, however, are limited in their scope and have been mostly used to elucidate specific areas of interest for which adequate data exist. There is now a need to provide a more systematic compilation of natural analogue data and illustrate by example their quantitative (or otherwise) use in safety performance assessment. This has been attempted through the initiative of the Finnish Power Company, Teollisuuden Voima Oy (TVO), who have contracted the Swedish Nuclear Fuel and Waste Management Company (SKB) to carry out an analysis of the application of natural analogues to performance assessment issues relevant to both TVO and SKB. In order to fulfil this assignment, SKB has formed a project group comprising personnel from SKB, Conterra AB and Kemakta Konsult AB.

It has been the ambition of the group to cover as broad a spectrum of performance assessment issues as possible, and to make the analysis of the issues technically specific when possible. It has, of course, been necessary to compromise between the depth of interpretation relating to individual topics and to the general scope of the whole project. There has not been the time or the resources to tackle all the issues as comprehensively as desired, so this report should be regarded as a starting point within an area of increasing interest to the scientific community, the regulators, independent peer review bodies and the general public at large.

The report presents not only a compilation of analogue applications already reported in the literature, but also the presentation of new performance assessment related issues and their quantitative evaluation. This report differs from the recent review by *[Miller et al., 1992]* entitled "Natural analogue studies in the geological disposal of nuclear wastes" in that actual performance assessment issues are being addressed. Some overlap is, however, inevitable, particularly with respect to the descriptions of the various analogue sites, the major analogue processes studied and the main results obtained. The main objective of this report is to go, albeit tentatively, one step further.

2. Basis for the work

A significant volume of data, potentially applicable to the problems of predicting repository performance assessment over long periods of time, are now available in the open literature as a result of studies pertaining to natural analogues and geological systems. These data have been sporadically used in performance assessments, notably within the Swedish and Swiss radioactive waste programmes, but there still exists a sizeable gap between the amount of money and effort put into the geoscientific studies compared to the effort and interest spent on applying such studies to performance assessments. This is partly due to historical reasons whereupon performance assessors tend to represent the engineering and chemical engineering fraternities and, as such, have concentrated on the performance of the near-field technical barrier systems which can be conveniently tested under laboratory conditions. With the onset of natural analogue and geological system studies, however, the reliability of laboratory data gave way to the uncertainty of complex field-derived data. As a result, existing models were either too simple or not robust enough to cope. On the other hand, perhaps field-derived data are inadequate for modelling purposes due to poorly analysed samples or inadequately defined boundary conditions etc., thus reflecting a failure of the geoscientist to recognise the type and quality of information required for performance assessment purposes.

Some progress has been made over the past 7 years or so to narrow this gap between the geoscientists and the performance assessors, e.g. through the Natural Analogue Working Group (NAWG) run under the auspices of the Commission of the European Communities, and within the international INTRAVAL project on model validation which is managed by the Swedish Nuclear Power Inspectorate in cooperation with the Nuclear Energy Agency of OECD. This present report attempts to further these aspirations by, in practice, systematically evaluating published analogue data and applying them to relevant performance assessment issues considered important to the TVO and SKB radioactive waste programmes. An attempt is also made to judge the usefulness of the data in performance assessment and to make recommendations that may improve both the focussing of future analogue/geological system studies and the appropriateness of present performance assessment models.

2.1 Performance assessment issues analysed

The group has listed a number of issues of relevance in the performance assessment work which have already been addressed in various published natural analogue studies. In setting up this list, the ambition has been to cover as broad a spectrum of topics as possible at the expense of interpretative detail for each individual issue. The following issues were identified:

General geochemical issues:

- Functional dependencies of groundwater redox conditions
- Validation of thermodynamic solubility codes and databases

Near-field related issues:

- Radionuclide transport in the near field of a repository
- Oxidation by radiolysis
- Formation and propagation of redox fronts
- Coprecipitation between radionuclides and other substances such as corrosion products

Far-field related issues:

- Radionuclide transport in the far field
- Channelling in conjunction with (radionuclide) transport
- The role of matrix diffusion in radionuclide transport
- The role of colloids in radionuclide transport

Miscellaneous:

- The potential role of microbes in performance assessment
- Analogues of construction materials
- The effect of glaciation on repository performance

As pointed out in the previous chapter it has been necessary to limit the depth of the analyses of the individual issues in order to be able to complete the work within the resources available. The depth of analysis varies considerably between the different issues and ranges from compilation of published analysis to original work in terms of quantitative analysis of available data.

2.2 Brief description of natural analogues evaluated

2.2.1 General

This section sets out to describe the natural analogues included in the present project. A brief description of the site, the main objective of the analogue studies and the main features used to fulfil the objectives are given. In addition to the natural analogue projects described below, the present project has utilised information from general observations and site investigations in different geological systems in various countries. This information is described in the context where it is analysed.

2.2.2 Poços de Caldas

The international Poços de Caldas project *[Chapman et al., 1992]*, located near the town of Poços de Caldas, Minas Gerais, Brazil, involved the study of several repository-linked processes which included redox-front movement, matrix diffusion and radionuclide migration. The project, conducted from May 1986 to March 1990, was the result of cooperation between the Swiss National Cooperative for Radioactive Waste Management (Nagra), the Swedish Nuclear Fuel and Waste Management Company (SKB), the U.S. Department of Energy (U.S.DOE), the U.K. Department of the Environment (U.K.DoE) and the Urânio do Brasil mining company. The field work concentrated on two sites; the Osamu Utsumi open pit uranium mine (Figure 2.1) and the Morro do Ferro prospect for thorium and rare-earth elements (Figure 2.2). Both sites are located in the Poços de Caldas caldera which is 30 km in diameter and consists of a Cretaceous alkaline volcanic complex formed some 75 Ma ago.

The host rocks *[Schorscher and Shea, 1992]* comprise a suite of hydrothermally altered intrusive bodies of nepheline syenites and flows of volcanic to subvolcanic phonolites which initially had relatively high background contents of uranium, thorium and lanthanides. Subsequent episodes of hydrothermal activity has resulted in the remobilisation of these elements causing local concentrations within the caldera, some of sufficient economic value such as at Osamu Utsumi and Morro do Ferro. The mineralisation at Osamu Utsumi consists mostly of low temperature pitchblende (mostly supergene in origin) with subordinate amounts of Mo, Zr, Th and REEs. At Morro do Ferro Th and REEs (mostly associated with resistate minerals) dominate with subsidiary amounts of uranium *[Waber et al., 1992; Waber, 1992]*.

Today the Poços de Caldas caldera is located 1 500 m above sea level, about 500 m below the level after its formation. The erosion rate has been calculated to be around 6-7 m per Ma for the last 50 Ma or so *[Holmes et al., 1992]*. The drainage pattern has, however, not changed much during that period. The weathering rate has been estimated to 12 m per Ma for the last 10 Ma.

Osamu Utsumi

General Features

The Osamu Utsumi uranium mine, in operation from 1975 to 1990, consists of an open pit covering an area of two square kilometres *[Waber et al., 1992]*. The rock consists of hydrothermally altered phonolites and nepheline syenites with the greatest concentrations of hypogene uranium (pitchblende with subordinate uraninite) located within two breccia pipes which formed the major conduits for the mineralising hydrothermal fluids. Within the weathered zones, affecting both the breccia pipes and host syenites and phonolites, the uranium has been remobilised to form supergene uranium deposits of pitchblende. In addition to uranium there are considerable amounts of subsidiary thorium, lanthanides, molybdenum and zirconium.

The investigations carried out were facilitated by the drilling of three shallow percussion (10-15 m) and five deep cored boreholes (55-300 m). Drillcore and surface mine samples were characterised mineralogically, geochemically and isotopically and groundwater samples collected from predetermined isolated borehole sections were analysed for major and trace elements and environmental isotopes; splits were used to extract colloidal and microbial material. Groundwater redox potential (E_h) and pH were measured in the field using the same equipment to that used up to 1983 on the Swedish site-specific study areas. The hydraulic data were used to model the flow conditions prior to and after excavation of the open pit mine.

Essentially, a similar detailed approach to a site-specific programme of investigation was applied at Poços de Caldas. Thus, indirectly, this analogue study proved to be a training and testing ground for site-specific techniques and methodology.

Hydrogeology

The hydrogeological studies *[Holmes et al., 1992]* show the site to be influenced by the extensive excavations which have extended the size of the areal groundwater discharge. This means that much of the bedrock which originally received downward-percolating oxidising waters now receives upward-discharging waters of a more reducing character. This is supported by: a) the hydrogeochemical studies which indicate active circulation (and marginally oxidising conditions) down to at least 50 m, and more reducing conditions extending to greater depths, and b) the tritium and stable isotopic data.

Hydrogeochemistry

In general, the groundwaters sampled are of unusual dilute composition and indicate intensive weathering from actively circulating fresh groundwaters in contact with the highly leached potassic-rich bedrock producing waters of K-Fe-SO_4 character *[Nordstrom et al., 1992]*. Uranium concentrations are generally high (up to 10 mg/L in the near-surface and <3 mg/L at depth) and thorium concentrations very low (<0.1 μg/L). Widespread disequilibria of $^{234}U/^{238}U$ characterises the groundwaters, and there is an inverse relationship of uranium concentration and the $^{234}U/^{238}U$ activity ratio with depth consistent with established redox and groundwater flow models. The REE concentrations in the groundwaters are typically in the range of 0.1-15.0 μg/L (LREEs) and 0.001-0.15 μg/L (HREEs), with higher contents in the near-surface waters in common with thorium.

Redox Fronts

The most spectacular feature of the Osamu Utsumi mine are the presence of redox fronts formed in association with the supergene uranium mineralisation. The fronts tend to penetrate to greater depths along hydraulically active fracture zones and within horizons of enhanced porosity, creating an irregular fingering pattern, Figure 2.3 *[Romero et al., 1990]*. They have resulted from the infiltration of oxidising water containing dissolved uranium into an otherwise reduced rock environment. In the reduced zone iron is mostly present as pyrite. When coming in contact with oxygenated water the pyrite is oxidised to Fe-oxyhydroxides (i.e. a Fe^{2+}/Fe^{3+} change) resulting in sharp (mm) colour changes from yellow/brown to green/blue-grey. This change, together with the very sharp increase in uranium concentration immediately inside the reduced section of the rock, indicates that the redox-controlled reactions affecting uranium occur at effectively the same place as those affecting iron.

The enrichment of uranium at the redox front is often as nodules of pitchblende on the reducing side (advection processes) or as sorptions onto the Fe-oxyhydroxides on the oxidising side (diffusion processes). Commonly on the reduced side of the fronts secondary pyrite forms, which is morphologically and isotopically distinct from the original primary pyrite. Locally, a clay-rich (kaolinite) layer may be observed at the redox front. In addition to the redox front, a less obvious hydrolytic front can be identified which defines the limit of rock alteration by near-surface fluids (weathering).

Whole-rock trace element analyses and U-decay series measurements show enhancements of trace elements around the redox fronts and some general geochemical trends can be observed *[MacKenzie et al., 1992]*. Symmetrical elemental and isotopic profiles across the fronts suggest that solute transport over the front may occur predominantly by diffusion or any advective transport that is occurring will tend to take place in the plane of the front at these locations. The natural series measurements showed that of the three fronts studied, one was concluded to be static (on a cm scale) and the other two were consistent with rates of movement in the range of 2-20 m in 10^6 a, in good agreement with 10 m in 10^6 a estimated from the regional erosion rates *[Holmes et al., 1992]*.

Microbiological analysis and modelling *[West et al., 1992]* suggest significant biological activity at the front; this was supported by S-isotopic data on secondary pyrites separated from nearby pitchblende nodules which indicated a microbial origin.

Plutonium and uranium were measured from a pitchblende nodule selected near the redox front. The Pu/U ratio suggests that the two elements have resided unfractionated in the deposit for the last 10^6 a, indicating a closed geochemical system *[MacKenzie et al., 1990]*.

Morro do Ferro

Morro do Ferro, some 5 km north of the Osamu Utsumi mine, forms a rounded hill of diameter about 1 km and, at 140 m above the plateau base level, constitutes the highest part of the Poços de Caldas caldera. Two streams drain the hill; one to the north and one to the south. The ore body, which was detected in the early 1950s during airborne radiometric surveys of the region, is located directly below the surface on the southern flank of the hill summit. It comprises mostly thorium and rare-earths with only subordinate concentrations of uranium, Figure 2.5. The mineralisation covers an area of approximately 150 × 320 m and extends to some 30 m depth; sporadic concentrations of thorium and rare-earths continue down to 100 m depth. Thorium contents range from 0.1-3 wt.% and rare-earths from 1-20 wt.%.

Morro do Ferro is believed to represent a highly weathered carbonatite complex intruded into host phonolites typical of those described from the Osamu Utsumi mine *[Waber, 1992]*. The ore body is believed to represent the accumulated residual weathered products of the carbonatite, i.e. concentrations of resistate accessory minerals rich in Th and REEs such as monazite, cheralite, thorite and pyrochlore. Dissolution of the more soluble primary mineral phases and accumulation of these resistate accessory phases has been facilitated by a stockwork of magnetite dykes and breccia, which are believed to comprise the most hydraulically conductive zones. Much of the uranium and some of the thorium is also associated with weathering products such as iron and aluminium hydroxides and clay minerals (gibbsite, illite and kaolinite).

Within the framework of the project a total of four new vertical boreholes were made with depths varying between 40 and 75 m; these complemented a series of shallow piezometric holes drilled in the early 1980s to evaluate the near-surface hydrology. The new holes were drilled along the hydraulic gradient determined largely by the major dyke pattern within the magnetite stockwork. The main objective was to ensure groundwater sampling locations at regular positions and at varying depths extending from the mineralisation near the summit to groundwater discharge at base level (i.e. the south stream). Hydraulic testing and conceptual modelling of the groundwater flow system followed by groundwater sampling (in association with the extraction of colloidal and microbial material) and rock sampling were performed along this profile. Sampling techniques and analytical methods were similar to those used at the Osamu Utsumi mine.

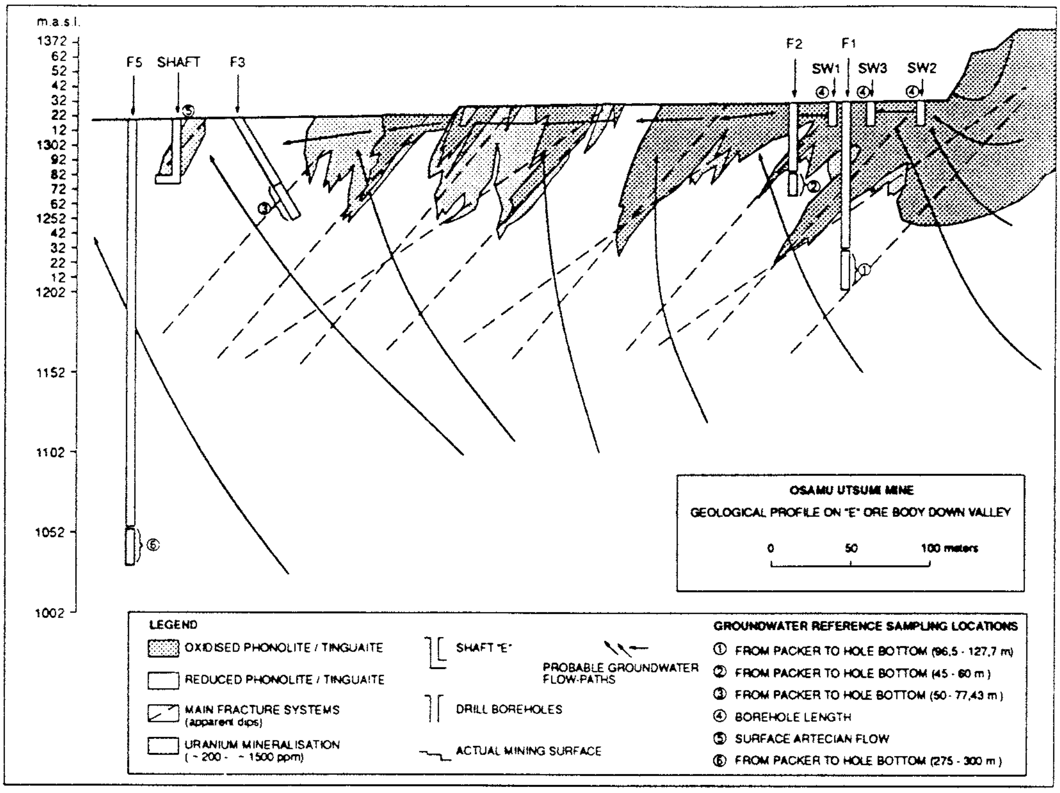

Figure 2.1 Section through the Osamu Utsumi uranium mine showing sample locations in relation to the geology, geochemistry and hydrology of the site (from *[Chapman et al., 1992]*).

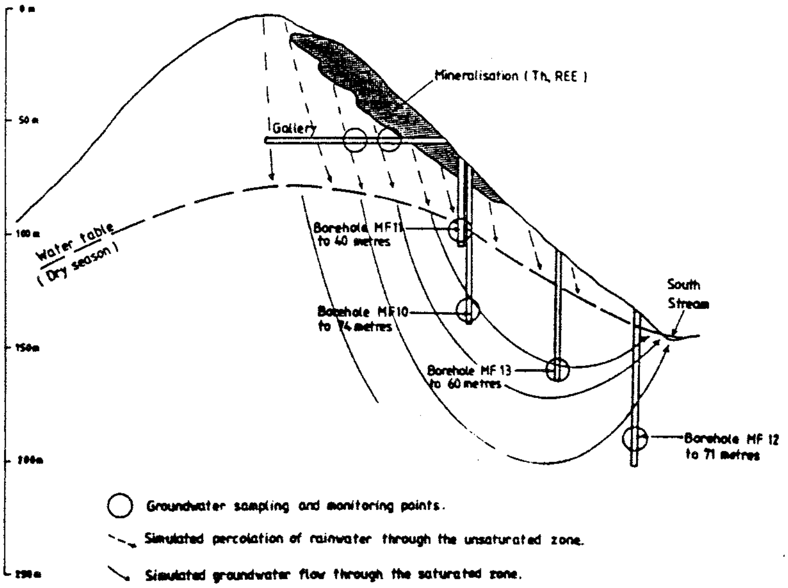

Figure 2.2 Section through Morro do Ferro showing groundwater/colloid sampling locations in relation to the mineralisation and the groundwater flow gradient (from *[Chapman et al., 1992]*).

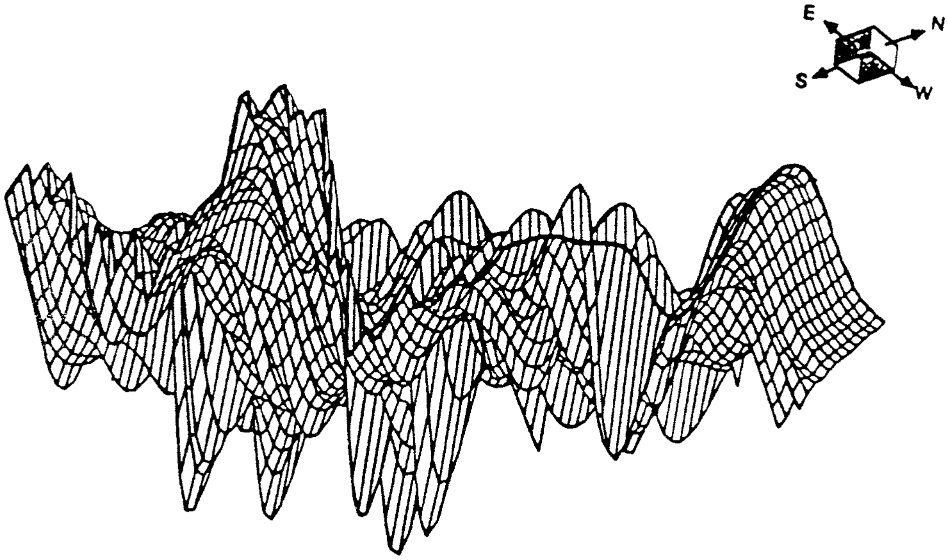

Figure 2.3 View of the geometry of the redox front in the Osamu Utsumi mine (from *[Romero et al., 1990]*)

A major advantage of Morro do Ferro over the Osamu Utsumi mine was the unperturbed nature of the groundwater system. Special emphasis was therefore put on the rock/water interaction modelling exercises and, in particular, colloid studies which formed a major part of the programme at this site. Hydrogeochemical studies showed similar groundwater chemistries to Osamu Utsumi and the hydrogeological model was supported by the environmental isotopic signatures.

Colloids

Particulate material was isolated from both shallow and deep groundwaters using sequential ultrafiltration techniques *[Miekeley et al., 1992]*. Low concentrations (<mg/L) of colloids, composed mainly of ferric oxyhydroxides and humic species, were found in the deep waters (also at the Osamu Utsumi mine). In association were only minor amounts of uranium but significant amounts of Th and REEs: uranium isotopic ratios in solution and of the colloidal material were similar. Colloidal organic carbon is common in the near-surface waters, where it complexes strongly with polyvalent metals, particularly Th and REEs. Suspended particles (>450 nm) have U, Th and REEs concentrations which are orders of magnitude higher than the associated colloid/true solution fractions. However, these larger particles, present in much smaller concentrations, are apparently immobile, and therefore do not appear to play any major part in Th and REE transport.

As a general conclusion, radionuclide transport (and other trace elements) by particulate material in deep groundwaters does not play any significant role in the geochemical processes of weathering, dissolution and erosion of these ore deposits. The main reason is that the weathered bedrock at Morro do Ferro acts as a very efficient filtering mechanism to particulate material.

Microbes were also analysed but no influence on radionuclide transport was noted.

The Natural Analogue.

The project had four main analogue objectives with respect to repository performance assessment *[Chapman et al., 1992]*:

- To assist in the validation of hydrogeochemical equilibrium thermodynamic models, codes and databases which are used to evaluate rock/water interactions and the solubilities and speciation of elements, using information from environments rich in rare-earth elements and natural series radionuclides.
- To determine the interactions of natural groundwater colloids, radionuclides and mineral surfaces with respect to radionuclide transport processes and colloid stability.
- To produce a model of geochemical transport across redox fronts, with special attention to the understanding of long-term, large-scale movements of redox-sensitive natural series radionuclides (including, if possible Pu and Tc).
- To model the migration of rare-earth elements and uranium-thorium series radionuclides during hydrothermal activity similar to that anticipated in the very near-field of some spent-fuel repository projects.

The studies at the Osamu Utsumi mine covered all four objectives; at Morro do Ferro studies focussed on the first two objectives. The fourth objective is not discussed in this report as it concerns temperature ranges in excess of those expected from the SKB and TVO disposal concepts.

2.2.3 Cigar Lake

The Cigar Lake analogue project has been in progress under the direction of the Atomic Energy of Canada Ltd. (AECL) since 1984. Collaboration between SKB and AECL extended for a three year period (1989-1992), and the US DOE have been involved since 1991. Presently data are being compiled, interpreted and documented with a joint SKB/AECL publication due early in 1993. An overview of the project is presented by *[Cramer and Smellie, 1993]*.

The SKB/AECL programme comprised the following tasks:

- Rock mineralogy and chemistry
- Ore mineralogy
- Radiolysis
- Nuclear reaction product geochemistry
- Hydrogeology
- Hydrogeochemistry
- Colloids
- Organic geochemistry and microbiology
- Model calculations

In addition to these tasks, three reference data sets were produced for integrated modelling purposes: groundwater analyses, rock mineralogy/geochemistry and a conceptual groundwater-flow model.

General Features

Geology/mineralogy

The Cigar lake uranium deposit, of hydrothermal origin and Proterozoic in age, is located in northern Saskatchewan at the southwestern edge of Waterbury Lake *[Fouques et al., 1986; Bruneton, 1985, 1986]*. It is one of many unconformity-type uranium deposits which characterise the Athabasca Basin uranium province, some of which consist of very high grades reaching several percent or even tens of percent of uranium. Compared to the other uranium occurrences (e.g. Cluff, Rabbit and Key lakes), Cigar Lake is notable because it is located entirely below the surface.

The ore deposit, comprised primarily of uraninite and pitchblende with subordinate coffinite, formed about 1.3 Ga ago *[Rudzicka and LeCheminant, 1986]*, and now lies at a depth of about 430 m at the unconformity of the Athabasca Sandstone Formation and the Archean basement complex. The average grade of the ore is around 12 wt% uranium with maximum concentrations up to 55 wt%. In common with the other major ore occurrences of the region *[e.g. Dahlkamp, 1978; Dahlkamp and Adams, 1981]*, which tend to form long linear deposits that straddle or flank traces of graphitic matapelites subcropping at the unconformity, Cigar Lake consists of an irregularly-shaped lens about 2000 m long, 25 to 100 m wide and 1 to 20 m in thickness. The present ore reserve has been calculated to 1.5×10^5 Mg U.

The ore is typically polymetallic in nature, the uranium being accompanied by a broad suite of elements including Ni, Co, Mo, Pb (radiogenic), Zn, Mn, Fe and V. The ore zone, in addition, is characterised by a clay-rich matrix dominated by illite and chlorite with minor carbonates (siderite and calcite) and accessory phases (e.g. zircon, rutile phosphates). Three stages of hydrothermal mineralisation can be recognised: a) euhedral uraninite and pitchblende associated with primary As-S minerals of Ni, Co and Fe, b) pitchblende associated with secondary As-S minerals in addition to Cu, Mo and Pb-S phases, and c) pitchblende associated with Fe-oxyhydroxides. The first stage has supplied the bulk of the Cigar Lake mineralisation. Subsequent low-temperature mobilisation (approx. 200-300 Ma ago) of the primary constituents has occurred on a local and less economic scale above (perched mineralisation along fractures) and also below (basement mineralisation) the primary ore body.

The ore deposit (Figure 2.4) is surrounded by a thick (5 to 30 m) clay-rich halo, consisting mostly of illite, kaolinite and quartz, with minor accessory minerals including rutile. At the ore/massive clay interface there often occurs a rich Fe-oxyhydroxide zone which decreases in intensity with distance from the contact (Figure 2.5). Surrounding the clay halo are hydrothermally altered sandstones (clay rich) which eventually grade via a quartz-cemented cap to unaltered sandstones which dominate to the bedrock surface. The altered sandstone is characterised by its white colour and the presence of iron sulphide (pyrite), which contrasts with the iron oxide (hematite) of the unaltered reddish sandstones.

The hydrothermal fluids which were responsible for the alteration of the basement and the sandstone host rocks, and producing the uranium mineralisation, were reducing when discharged from the basement into the sandstone along fracture conduits of regional character. These fluids interacted with downward percolating oxidising uranium-rich meteoric groundwaters in the sandstone, and this resulted in the mass precipitation of uraninite and pitchblende. Alteration of the host sandstone involved the dissolution of hematite (colour change from red to white) and an increase in the clay content. This sandstone clay content, particularly within the quartz-rich cap, increases markedly towards the ore zone due to the more efficient dissolution of the rock matrix by the hot discharging hydrothermal fluids. Such alteration processes are typical of the unconformity-type deposits of the Athabasca Basin *[Hoeve, 1984]*.

The metamorphic basement at Cigar Lake is mainly composed of fine-grained metapelites with intercalations of calc-silicate gneisses; the uranium deposit is underlain by augen-textured metapelites initially rich in graphite. Palaeoweathering of the pre-Athabasca basement resulted in a regional alteration of the regolith down to around 50 m producing a general breakdown of the metamorphic mineral assemblage to illite, kaolinite and chlorite *[MacDonald, 1980]*. Penetration of the hydrothermal fluids upwards through the augen-textured graphite-rich metapelites resulted in a complete alteration and superimposition of a hydrothermal sequence of mineralogy and geochemistry on the fine-grained pelites and calc-silicate gneisses which flank the augen-textured metapelites. At the base of the mineralisation, the pre-Athabasca regolith has been completely altered *[Bruneton, 1985]*.

Hydrogeology

[Winberg and Stevenson, 1992] developed 2D and 3D models of the Cigar Lake uranium deposit both on a regional and local scale. Maps were produced of hydraulic head, particle velocity and particle tracks and sensitivity analyses were carried out on the boundary conditions, the geometry of the uranium deposit and the rock material properties. The schematic 2D vertical section through the Cigar Lake deposit based on the 3D local model is illustrated in Figure 2.6. Three major flow regimes are shown: local flow regime I characterising the overburden, intermediate flow regime II restricted to the Upper Sandstone Formation and deep semi-regional regime III restricted to the Lower Sandstone Formation. Some hydraulic interconnection occurs between each regime by minor fracture percolation and flow along major conducting fracture zones. Inserted on the figure are calculated particle velocities, v_p. Note the very low particle velocities predicted in and around the deposit and the underlying basement, compared with the surrounding rock units.

The calculated residence times in the ore/clay zone for particles released within the ore vary between 18 000 and 85 000 a. These values correspond closely with groundwater residence times calculated from ^{36}Cl data.

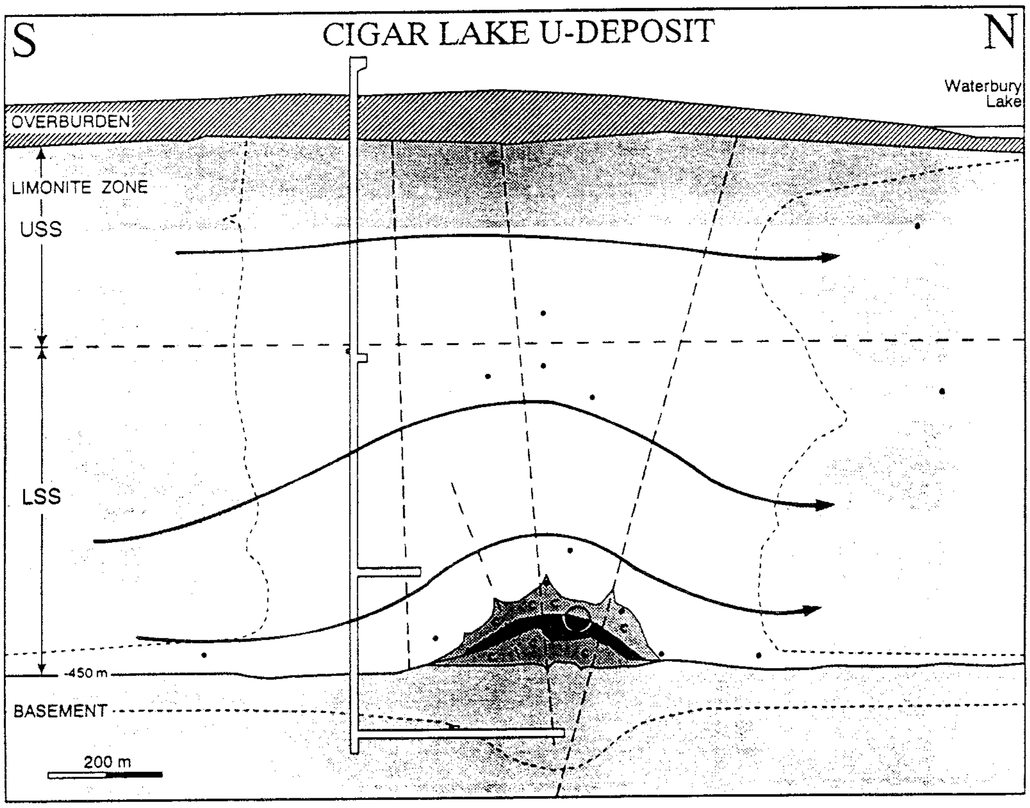

Figure 2.4 Schematic vertical profile through the Cigar Lake uranium deposit showing the major rock units, the clay (c) and ore (black) zones, the vertical shaft and the main groundwater flow directions (modified after *[Vilks et al., 1991]*).

Figure 2.5 Profile from the massive clay showing the colour change from the clay/ore contact (grey/black) grading through to the Fe-oxyhydroxide/hematite clay (red) to eventually the bleached (white) clay *[SKB's archive material]*.

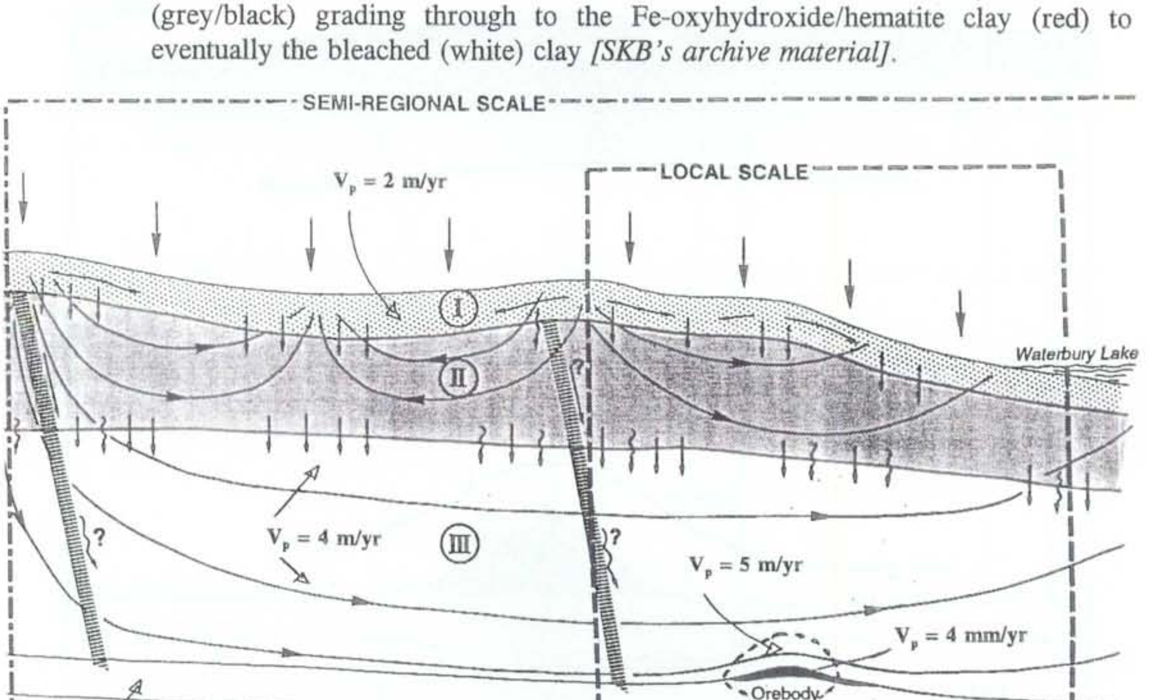

Figure 2.6 Schematic vertical 2D section through the Cigar Lake deposit showing defined flow regimes and their interaction; see text for explanation (from *[Winberg and Stevenson, 1992]*).

Hydrogeochemistry

The geochemistry and evolution of groundwaters at Cigar Lake are described in detail by *[Cramer and Nesbitt, 1993a-c]*. In general, groundwaters in and around the uranium deposit are characterised by neutral to near-neutral pH (~6-8), by having low contents of total dissolved solids (~60-240 mg/L), by decreasing redox potentials toward the ore zone (from ~+25mV to ~-25 mV), and by overall low uranium contents (<30 μg/L or $10^{-6.5}$ mol/L). Within the ore-zone groundwaters, marked increases in the contents of certain nuclides (e.g. ^3H and ^{36}Cl) are observed as a result of nuclear reactions occurring in situ.

The conceptual hydrogeochemical model for the evolution of water compositions at Cigar Lake is illustrated by the redox diagram in Figure 2.7. This evolution is characterised by interaction of the waters primarily with the clay and iron minerals in the rocks. Surface precipitation (rain and snow) reacts with illite and kaolinite dissolving iron from various minerals in the overburden and producing a recharge water to the Upper Sandstone unit that is already equilibrated with the main clay minerals and that is rich in iron (point **A** in Figure 2.7). Reaction of this oxidising recharge water with the Upper Sandstone produces precipitation of Fe-oxyhydroxides down to a depth of about 100m, overprinting both the unaltered and the bleached sandstone ("limonite" zone; **B** in Figure 2.7). Upon approaching the clay and ore zones of the deposit, subsequent reaction of the waters with Fe-sulphides and siderite in the bleached sandstone reduces the oxidation potential of these waters (decreasing pO_2: **B→C→D/E** in Figure 2.7) to well within the UO_2 stability field. The redox-buffering capacity of the Fe-sulphides in the ore and its host rocks plays an important role in maintaining reducing conditions and, thus, preserving the stability of the uranium mineralisation.

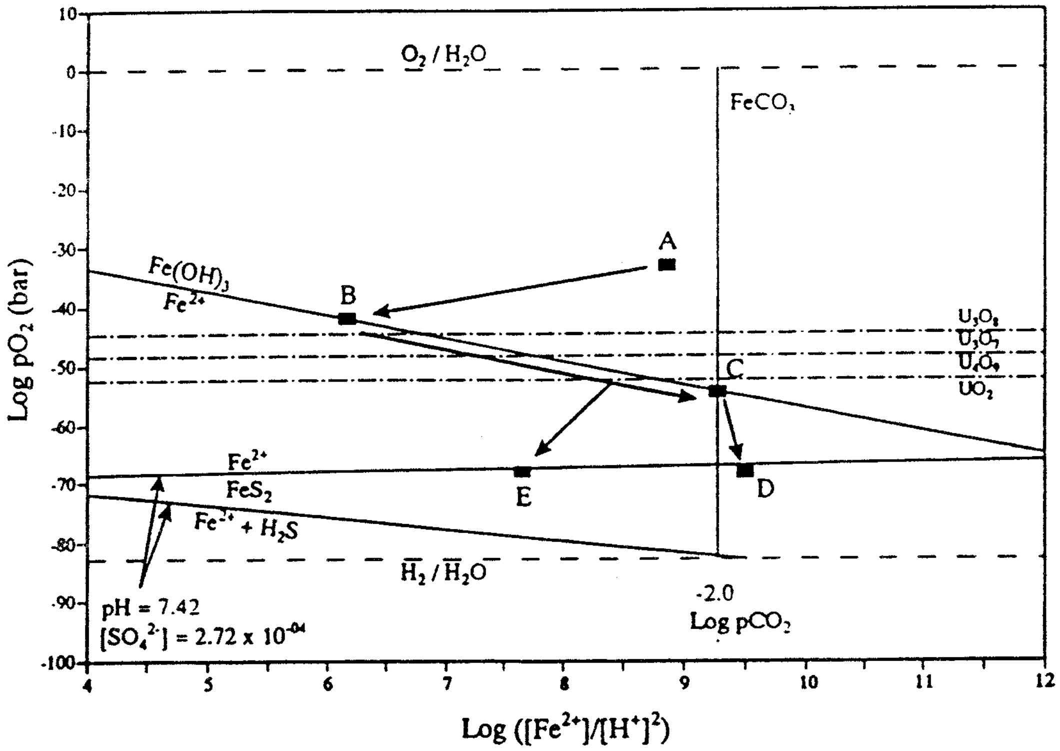

Figure 2.7 Redox diagram for water-rock interaction in the Cigar Lake deposit. Groundwater compositions evolve from **A** (overburden) to **B** (unaltered sandstone and limonite zone), to **C** (altered sandstone). Semi-dashed lines represent stability boundaries for various solid uranium oxides (from *[Cramer and Nesbitt, 1993b]*)

Colloids, Microbes and Organics

In parallel with groundwater sampling for hydrogeochemical characterisation, sample splits were collected for the separation of colloid, microbial and organic material *[Vilks et al., 1991; Pettersson et al., 1992]*.

Colloid studies involved not only a chemical and physical characterisation of colloid material, but experiments were also carried to study the effects of sample pump rate and borehole flushing on particle size, concentration and chemical/physical properties. Variation in particle concentration appeared to result from piezometer flushing rather than changes in the sample pumping rate, although given a sampling period, the colloid concentrations typically decreased with progressive sampling.

Suspended particle concentrations were found to reflect the local contact rock rather than the geological formation. With the exception of the two basement holes, colloid concentrations were found to be fairly uniform throughout the deposit. In the clay zone only one borehole, in contact with a fracture zone, recorded large amounts of suspended particles. The particles (>50 nm) consist primarily of clay minerals (illite, chlorite and kaolinite), x-ray amorphous Fe-Si precipitates, quartz and organic particles. The major ion chemistry reflects the mineralogy; trace elements such as uranium (and thorium and radium) show average values which are significantly higher for particles in the ore than in other parts of the deposit. However, the uranium concentrations of particles downstream from the deposit are no greater than the surrounding sandstones, showing that there is no "uranium plume" emanating from the orebody, i.e. the clay halo provides an efficient barrier. Uranium decay series measurements of the particles and the groundwater indicates that the uranium associated with the particles is most likely acquired from the groundwater because the $^{234}U/^{238}U$ ratios for dissolved and particulate uranium are similar.

The study of humic substances in the Cigar Lake groundwaters from the general sedimentary host rocks showed a total organic carbon (TOC) in the range of 0.6-0.17 mg/L (15-25% humics); this contrasts with the ore zone which recorded 10.6 mg/L (<2% humics). The humic fraction is mostly as low molecular weight fulvic acid. From the ore zone the extracted humic fraction was dated to >15 000 years (by ^{14}C); however, modern humics were also detected indicating exchange with recent waters.

Several bacteria have been identified in the vicinity of the orebody; those confirmed include sulphate-reducing, denitrifying, Fe-related and possibly methanogenic varieties *[J. Cramer, written comm. 1992]*.

The Natural Analogue

For some time many of the Cigar Lake features have been considered analogous to concepts being developed internationally for the disposal of nuclear fuel waste deep in crystalline rock formations *[Cramer, 1986; Cramer et al., 1987; Goodwin et al., 1988]*. To test present performance assessment (PA) concepts, the following PA-related objectives were defined *[Cramer and Smellie, 1993]*:

- assisting in the validation of equilibrium thermodynamic codes and databases,
- the role of colloids and organics in radionuclide transport processes (near- to far-field analogy),
- the influence of radiolysis on uranium ore (UO_2) dissolution and radionuclide transport (near-field analogy), and
- mass transport of dissolved radionuclides through the surrounding clay halo and their downstream dispersion from the deposit (near- to far-field analogy).

Contrary to Oklo, nuclear criticality was never achieved at Cigar Lake even though uranium concentrations are higher. This has been attributed to several reasons which include: a) its younger age; i.e. by the time the orebody formed, the natural $^{235}U/^{238}U$ ratio had decayed to too low a level to allow a critical mass to be reached, b) the presence of high amounts of poison elements (e.g. neutron-capturing nuclei such as boron and the REEs), and c) the clay barrier prevented ready access of hydrogen and water (i.e. neutron moderators).

Neutrons from spontaneous fission of uranium, however, continuously produce radioactive isotopes such as ^{3}H, ^{14}C, ^{36}Cl, ^{99}Tc, ^{129}I and ^{239}Pu. These amounts are measurable and commonly exceed present atmospheric levels. For example, the concentration of tritium in the ore zone is higher (> 100 TU) when compared to present bomb pulse tritium in near-surface groundwaters (~ 50 TU) from the Cigar Lake region.

2.2.4 Alligator Rivers

The Koongarra Uranium Deposit, in the Alligator Rivers Region in the Northern Territory of Australia, has been investigated within the international Alligator Rivers Analogue Project (ARAP) set up in 1987. The project is sponsored by the OECD Nuclear Energy Agency and the participants include the Australian Nuclear Science and Technology Organisation (ANSTO), the Japanese Atomic Energy Research Institute (JAERI), the Power Reactor and Nuclear Fuel Development Corporation of Japan (PNC), the Swedish Nuclear Fuel Inspectorate (SKI), the UK Department of the Environment (UK DOE) and the US Nuclear Regulatory Commission (US NRC).

The main objective of the ARAP is to study the Koongarra natural uranium deposit to assist in the long-term prediction of the rate of transport of radionuclides through the geosphere. Specific aims are to evaluate the significance of processes which may play an important part in radionuclide transport and to establish a radiochemical database. The ARAP will be finalised during 1992 and the results of the project are to be published in a series of 14 reports.

The technical programme comprises five major sub-projects involving both modelling and experimental work:

I Modelling of radionuclide migration
II Hydrogeology of the Koongarra uranium deposit
III Solid phase studies
IV Groundwater
V Fission product and transuranic nuclides

General Features

Geology/mineralogy

The Koongarra uranium mineralisation is one of four major uranium deposits which characterise the Pine Creek syncline which comprises about a 14 km thick sequence of Lower Proterozoic metasediments (carbonaceous pelites, psammites and carbonates) together with interlayered tuffs which were deformed and metamorphosed 1.8 Ga ago. These rest unconformably on the Archean basement and are, in turn, overlain by younger rocks of Middle Proterozoic age. The deposits themselves lie at the base of the Cahill Formation schists and are located in extensively chloritised zones and adjacent to massive dolomites.

The Koongarra mineralisation occurs in two distinct, but clearly related, orebodies separated by about 100 m of barren schist (Figure 2.8). The primary mineralisation was probably formed by hydrothermal activity approximately 1.6 Ga ago, and consists of uraninite- and pitchblende-bearing veins (associated with small amounts of sulphides and even some rare native gold) within a zone of steeply dipping, sheared quartz-chlorite schist. The Koongarra Reverse Fault brings the schist into contact with the Kombolgie sandstone, and forms the lower boundary (or footwall) to the uranium ore zone (Figure 2.9). A graphitic quartz-chlorite schist forms a distinctive hanging wall unit in the primary ore zone. The strongest mineralisation, with most assay values in excess of 1% U, has a thickness of several metres below the graphitic hanging wall schist unit.

The No 1 orebody, which is the subject of the ARAP, has a strike length of 450 m and persists to a depth of about 100 m (Figure 2.9). Alteration and weathering of the primary mineralisation have resulted in the formation of a tongue-like fan of secondary uranium minerals, mainly uranyl phosphates, in a zone extending from the surface down to the base of weathering at a depth of approximately 25 m. Secondary uranyl silicates are found within the top of the primary zone just below the base of weathering and at the bottom of the primary zone along and just above the fault (Figure 2.9). Uranyl phosphates minerals occur in the weathered zone, in and downslope from what was the upward extension of the primary ore zone as well as in the tail of the dispersion fan. Intersection of the zone of surface weathering with the top of the primary ore zone has resulted in the leaching and decomposition of both pitchblende and uranyl silicates to form the uranyl phosphates in the weathered zone. Away from the tail of the fan, uranium is dispersed in the weathered quartz-chlorite-schist and adsorbed onto clays (vermiculite, kaolinite, smectite) and iron oxides. The dispersion fan of ore grade material extends downslope for about 80 m to the south of the mineralisation. The transformation of the original primary mineralisation zones into the present secondary minerals is perceived to have taken place during well over a million years.

The upper extension of No.2 orebody is located about 30 m below the surface (Figure 2.8), which is below the base of weathering. Consequently, no weathering of this orebody has occurred and there is no known mobilisation of uranium. No.2 orebody has therefore not been further studied.

Uranium series data show that the areas of greatest leaching are near the upstream zone of the orebody. The most rapid accumulation seems to have occurred near the centre of the dispersion fan and near the base of the weathering to the edge of the fan. *[Edghill, 1991]* concluded that during weathering, uranium distribution follows the formation of various iron phases and that oxides of Fe and Mn appeared to dominate scavenging of the radionuclides. A large proportion of the total U was found to be associated with various Fe-rich phases *[Nightingale, 1986]*. Recently *[Koppi and Klessa, 1992]* have shown that within the Fe-rich areas (up to 60% Fe), U (<4%) is associated with Fe in a diffuse fashion. Within Mn-rich areas there were smaller areas with high concentrations of U (up to 17%) in intimate contact with Ce (up to 61%); this relationship may be crucial in understanding the dynamics of U movement and its redistribution.

Hydrogeology

Emphasis was initially focussed on the development of a 2D coupled groundwater flow, heat and solute transport, and chemical reaction model of the Koongarra uranium deposit *[Raffensburger and Garven, 1989]*. In this model a finite element model of flow in a vertical section was presented. Since then several different approaches have been attempted to model the Koongarra system; initially it was represented purely as a porous flow medium, but more recently a significant degree of anisotropy has been introduced into the models *[Townley and Barr, 1992; Smoot, 1992]*. *[Townley and Trefry, 1991]* have recently presented 2D and 3D modelling of the groundwater flow in vertical sections on a much larger regional scale, with the improved aim of identifying the real boundaries of the local flow system near the orebody. 3D modelling based on schistosity structures has also been recently attempted.

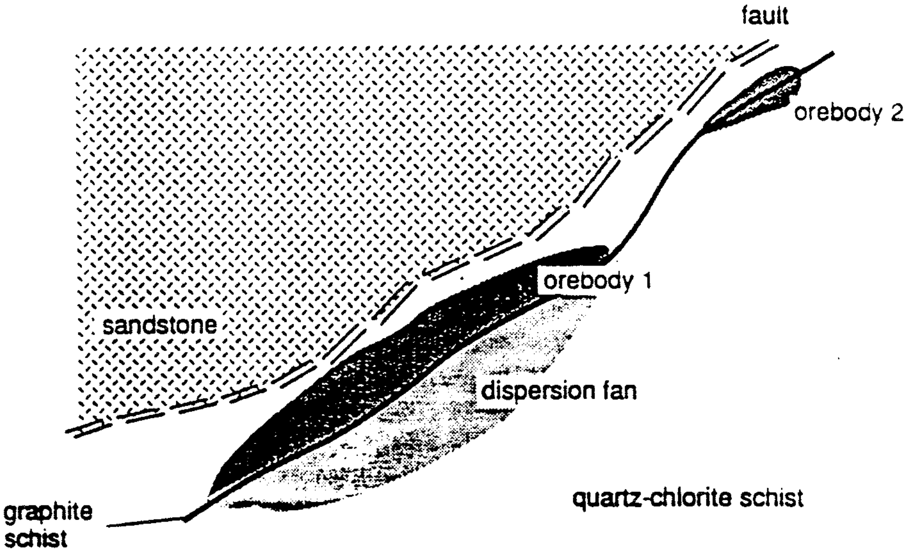

Figure 2.8 Planar view of the Koongarra orebodies projected onto the ground surface (from *[Duerden (Ed.), 1992a]*).

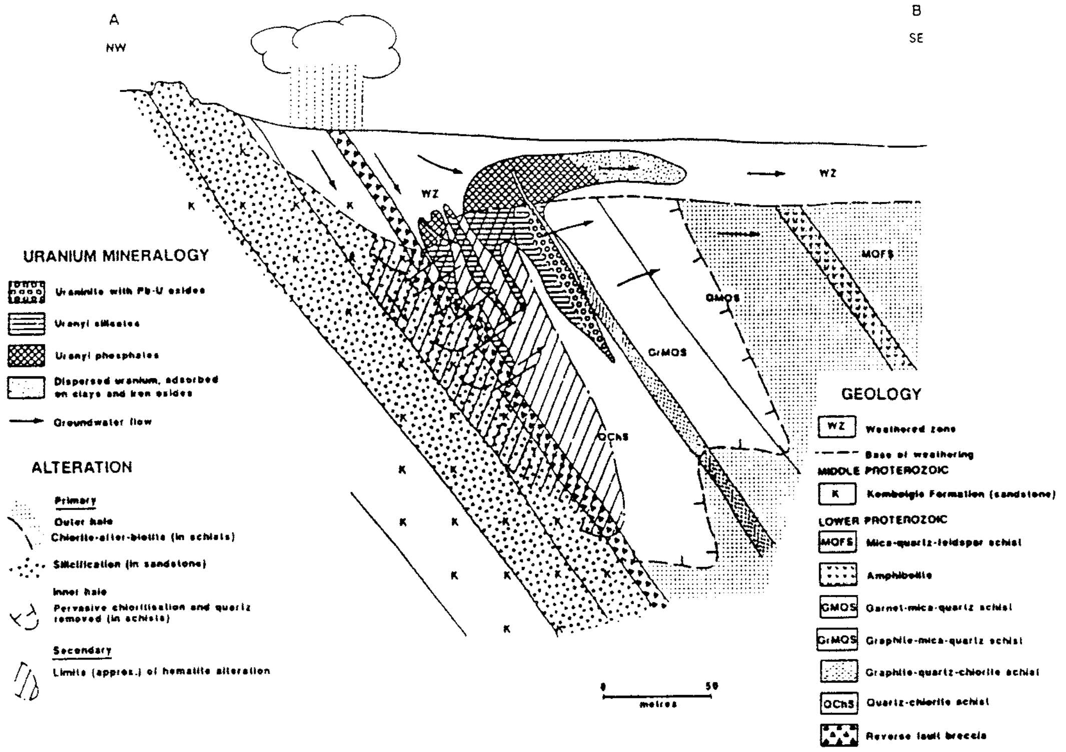

Figure 2.9 Simplified cross-section through the Koongarra No.1 orebody showing geology, distribution of uranium minerals, distribution of alteration and present groundwater flow directions (from *[Duerden (Ed.), 1992a]*).

There is no cohesive groundwater flow model yet available for the Koongarra uranium deposit. Previous modelling concentrated on an idealised profile allowing the flow, which originated beneath Mt. Brockman in the Kombolgie sandstone, to pass through the No.1 orebody. Nevertheless there is now general agreement *[Townley and Barr, 1992]* that:

a) most of the horizontal groundwater flow (excluding shallow flow in the superficial sediments) occurs at or below the bottom of the weathered zone (Figure 2.9). Essentially the system can be considered as a confined aquifer with horizontal flow below the weathered zone,

b) there is little evidence of significant flow across the Koongarra fault (Figure 2.9); even apparent reversals of gradient have been measured,

c) there appears to be a highly conductive zone to the SE of the No.1 orebody, and

d) the directions of flow are influenced by schistosity planes and sub-parallel fractures to these planes.

The concept of fracture-flow has been discussed by *[Smoot, 1992]* as being the most probable explanation of increased permeability within the aquifer. Fracture-flow is also supported by the basic geology and mineralogy of the site; mineralisation and secondary alteration products are largely confined to fractures and fissures which in turn must also determine the groundwater chemistry through rock/water interactions. 2D modelling of fracture-flow pathways is presently being conducted.

Hydrogeochemistry

Groundwater data are available for more than 70 boreholes positioned to collect water along the aquifer paths. Sampled groundwaters most frequently fall into three main groups: a) less than 15 m depth (middle of the completely weathered zone), b) between 23-26 m depth (transition to the unweathered rock), and c) 35-45 m depth (fresh schist ± incipient weathering). The various lithological units which comprise the mineralisation and its surroundings play an important role in establishing the character of the groundwater chemistry *[Sverjensky, 1992]*.

The upper shallow zone is affected seasonally, fluctuating between the rainy (saturated) and dry (unsaturated) periods; below 15 m the groundwater is apparently unaffected and is considered part of the regional groundwater flow pattern. In general, the groundwaters are all dilute waters (up to 150 mg/L TDS) and dominated by Mg and HCO_3; dissolved Si is a major constituent (0.5 mM). Cl is usually low although slightly higher than precipitation; this indicates a slight degree of evaporation of the recharge waters. Mg, Ca and HCO_3 are enriched relative to Cl suggesting mineral-solution reactions within the soil zone and within the aquifers themselves. Similarly, dissolved Si is a product of silicate hydrolysis *[Herczeg and Payne, 1992]*.

Depth trends show expected decreases in acidity (pH from 5.5 to 7.7) and redox potential (Eh from 400 to 100 mV) and increases in the major ionic solutes Mg and HCO_3. Most other anions, B, CL, SO_4 and F, show either no change with depth or slight increases. In contrast, PO_4 is essentially constant as a function of depth. According to *[Sverjensky, 1992]*, present-day groundwater compositions can be attributed mainly to vertical recharge by rainwater that progressively evolves chemically by reaction with the chlorite in the schist to form kaolinite.

[Herczeg and Payne, 1992], who have integrated hydrochemistry with environmental isotopic signatures, conclude that recharge occurs mostly during large events and there is continuous mixing of waters downstream with the groundwaters becoming more dilute and more enriched in ^2H and ^{18}O. $\delta^{13}C$ data indicate that most of the dissolved constituents are derived by the action of biogenic CO_2 on Mg silicates (chlorites) thus releasing Mg, HCO_3 and SiO_2 into solution, in agreement with *[Sverjensky, 1992]*.

Groundwaters within the Kombolgie sandstone are hydraulically connected to groundwaters across the fault zone but most of the weathering occurs downstream of the fault. Apparent ^{14}C ages appear to be an artifact of fluid and CO_2 dynamics within the groundwater system. Also, the addition of "dead" CO_2 of biogenic origin decreases in importance down-flow and leads to an apparent decreasing age along the transect.

Fission Products and Transuranics

Preliminary results indicate that Pu concentrations in the groundwaters are probably very low, on the order of 10^{-18} M or less. Only in the centre of the ore deposit, in the particulate fraction, has Pu been detected. However, Pu has been detected in the particulate and anionic fraction of groundwater sampled a few hundred metres away. In this latter case, the most probable source is global fallout of anthropogenic Pu.

Colloids

Studies have shown that colloid transport of radionuclides is relatively unimportant at Koongarra. U migrates mostly as dissolved species, whereas Th and Ac are mostly associated with larger, relatively immobile particles (> 1.0 μm). A significant amount of ^{230}Th, however, that passes through a 1.0 μm filter is associated with colloidal particles consisting mostly of Fe-oxides and clays and reflect the local mineralogy.

The Natural Analogue

The uranium ore deposit of Koongarra, with its inventory of radionuclides, provides researchers with an excellent system with which to study radionuclide migration over very long timescales, that can be related to repository design *[Duerden (Ed.), 1992b]*. One of the main objectives is to study the natural uranium deposit to assist in the long-term prediction of the rate of transport of radionuclides through the geosphere. It should then be possible to develop a consistent picture of the processes that have controlled transport in the Koongarra weathered zone and the time-scales over which they have operated.

In summary, the overall objectives of the Alligator Rivers Analogue Project are to:

- contribute to the production of reliable and realistic models for radionuclide migration within geological environments relevant to the assessment of the safety of radioactive waste repositories,
- develop methods of validation of models using a combination of laboratory and field data associated with the Koongarra uranium deposit, and
- encourage maximum interaction between modellers and experimentalists in achieving these objectives

To achieve these objectives, the following analogue processes have been studied: a) primary and secondary uranium dispersions in the rock matrix and in fractures, b) the role of groundwater and colloids in radionuclide transport, c) the production and dispersion of the fission products ^{129}I and ^{99}Tc, and transuranics ^{239}Pu, and d) the development of modelling codes and evaluation of the Koongarra Site for modelling studies.

2.2.5 Oklo

Since the discovery of ^{235}U-depleted uranium ore from the Oklo deposit in 1972, numerous studies have been conducted and the early results presented at two IAEA symposia in 1975 and 1977. Although both indirect and direct use has been made of Oklo data in the analogue context for the last 10 years or so (e.g. *[Curtis and Gancarz, 1983]*), it has only been recently in 1990 that a formal natural analogue project has been established ("Oklo as a natural analogue for deep waste disposal") under the joint auspices of the Commissariat a l'Énergie Atomique (CEA) and the Commission of the European Communities (CEC).

General Features

Geology/mineralogy

Uranium mineralisation in the Oklo/Okelobondo/Bagombé region initially resulted in early Proterozoic times from a partial remobilisation of uranium from uranium-bearing, Witwatersrand-type conglomeratic/sandstone placer deposits, initially derived from the erosion of the Challu massif of Archean age located to the south-west of the Francevillian Basin; these form the basal deposits of the Francevillian Sedimentary Series. Overlying these intercalations of conglomerates and sandstones (referred to as the "FA" Formation) are a thick series of marine-derived, organic-rich pelites associated with limestones (referred to the "FB" Formation). This organic matter subsequently matured to form hydrocarbons when burial temperatures approached 150°C. At a later stage, some 2.05 Ga ago, diagenesis of this sedimentary pack produced a partial remobilisation of the uranium reserves through the circulation of oxidising waters, accessed by widespread hydraulic fracturing. When these oxidising uraniferous waters came in contact with the reducing front of the organic matter, the uranium became concentrated in the sandstone sediments beneath the "FB" Formation. At Oklo/Okelobondo/Bagombé the mineralisation became established in a layer a few metres thick (referred to the "C1" layer), which forms a distinct marker horizon between the "FA" and "FB" Formations (Figure 2.10). This represents the bulk of the common ore presently being mined to-day, with an average concentration of 0.3-0.4% UO_2.

Reactor Zones

At present, all the known natural fission reactors (some 16 have so far been identified) are located in the Franceville Basin (Figure 2.11), although these are not only restricted to the Oklo/Okelobondo sector; the Bagombé reactor zone was discovered 20 km to the south-east. The reactor zones, and the Francevillian sediments as a whole, are well preserved, having undergone very little regional metamorphic alteration during the last 2 Ga or so.

The reactors are characterised by: a) high concentrations (20-60% U) of uranium ore (mostly uraninite) closely correlated to ^{235}U depletion of up to 0.265% of the total U, and b) fission products whose end-member isotopic compositions are very different from those of the natural elements. Figure 2.12 represents a schematic profile through reactor 2 showing the relationship between uranium content, % ^{235}U and the calculated neutron flux.

The reactor ores are usually, but not always, surrounded by a clay halo (illite + Mg-Al chlorite adjacent to core, the chlorite becoming more Fe-rich towards the surrounding normal sediments); quartz is largely absent (Figure 2.13). The clay features have been formed by the conversion of the original sandstone by thermal convective circulation of water, initiated by heat released during the nuclear reactions.

The reactor zones date from 1.75 Ga (based on isotopic disequilibria) to 1.97 Ga (based on neutron calculations), criticality in individual reactors lasted anything from 0.5 to 0.8 Ma, and temperatures reached a maximum of around 450°C during the reactions. According to *[Naudet et al., 1978 a,b]* the main factors initialising the nuclear fission reactions were: 1) a high uranium content, 2) a low content of poison elements (neutron-capturing nuclei such as boron and REEs), 3) the presence of light nuclei (neutron moderators) such as hydrogen and water, and 4) a high concentration of fissionable nuclei in the uranium. It has been calculated that criticality could have been achieved once the UO_2 concentration exceeded 11% over a thickness of 2 m in preferential locations such as faults, where there was an increase in porosity and, consequently, the availability of water. The reactions were terminated when the ^{235}U concentration and quantity of water were reduced as the porosity became progressively sealed through hydrothermally-induced argillisation of the surrounding sandstones.

The Natural Analogue

Offhand this deposit would seem to be an ideal analogue for a waste repository, a location where predictions about rates of movement of various radionuclides could be given a rigorous test. Although the source-term chemistry at the site might be expected to be similar to that resulting from the leaching of high-level waste, quantitative analysis of this system is extremely complex due to uncertainties in the geochemical and hydrothermal history of the region. Analogue investigations have been focussed primarily on the stability of the UO_2 (spent fuel analogy), the transport and retardation of fission products, actinides and actinide daughters, and the effects of radiolysis.

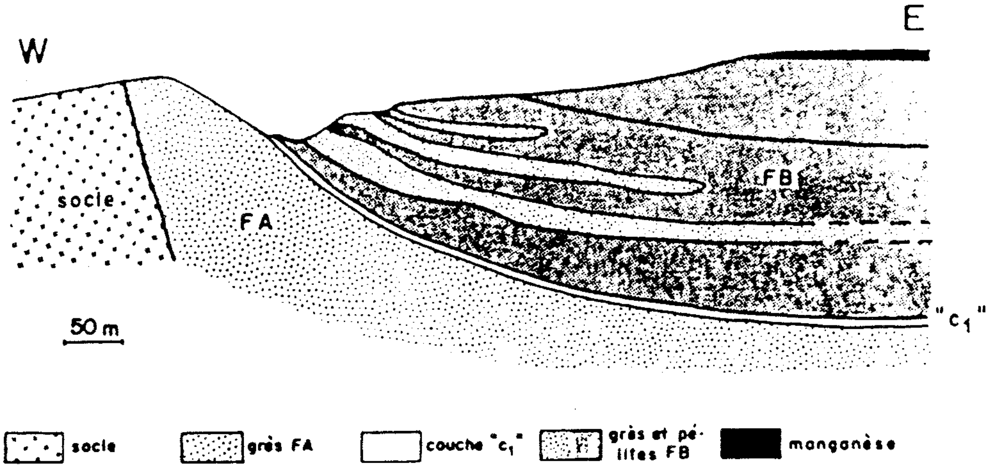

Figure 2.10 Schematic profile across the Oklo open-pit showing the position of the "C1" layer of pelitic sediments which host the presently mined uranium ore and the reactor zones.

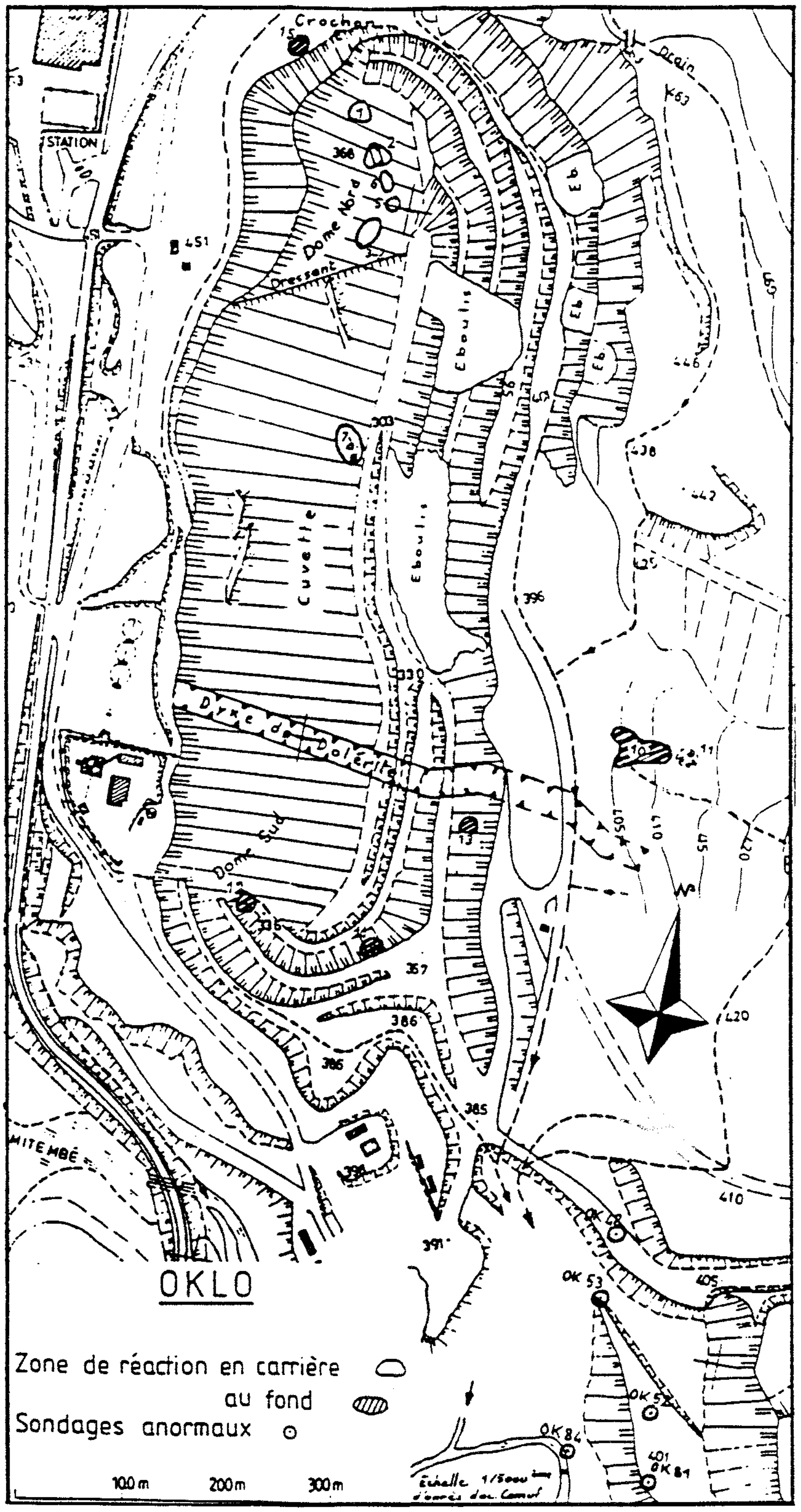

Figure 2.11 The Oklo open-pit showing the locations of reactor zones 1-15; reactors 10 and 13 to the east are underground, in the near-vicinity of the dolerite dyke, and are presently under investigation. Okelobondo is the area extending south from the southern edge of the open-pit (from *[Blanc et al., 1988]*).

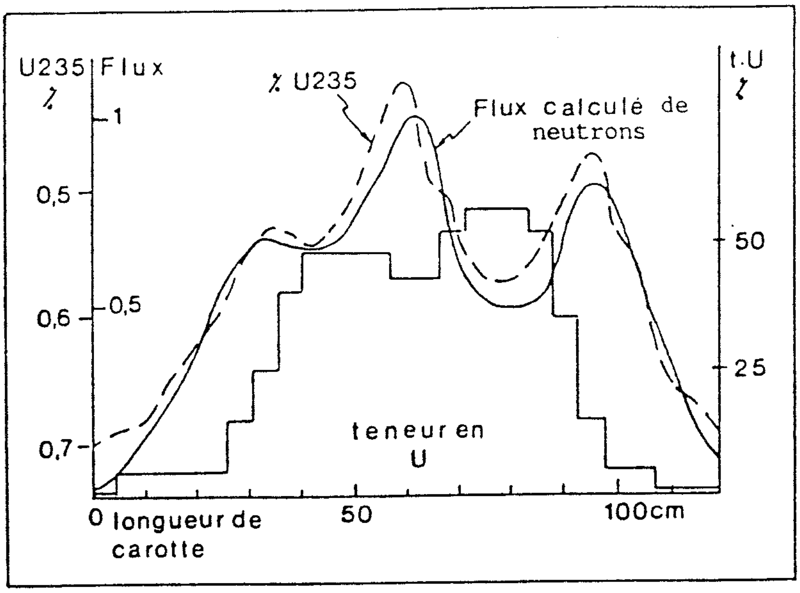

Figure 2.12 Schematic profile through reactor 2 (see Figure 2.11 for location) showing the relationship between U-content, %^{235}U and the calculated neutron flux (modified after *[Naudet and Renson, 1976]*).

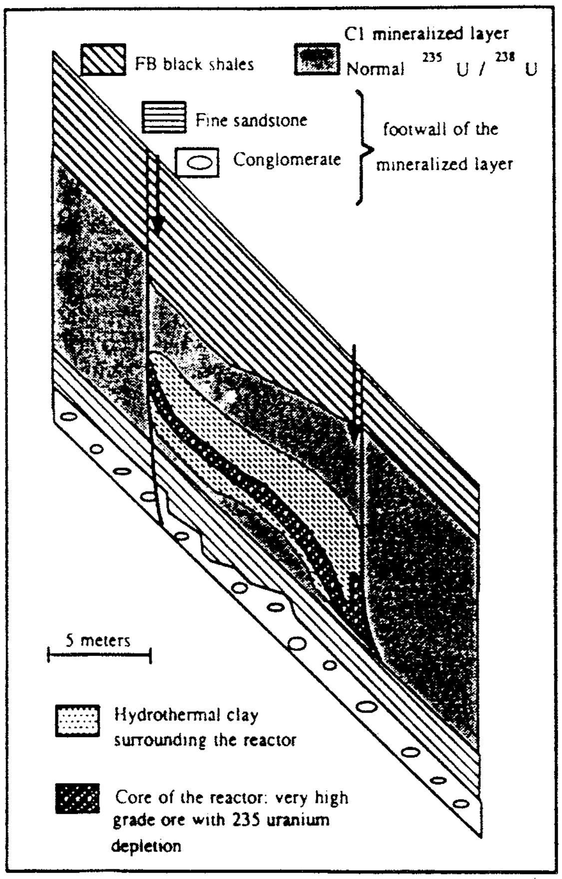

Figure 2.13 Schematic profile through a natural fission reactor at Oklo. (from *[Gauthier-Lafaye et al., 1989]*).

Spent Fuel Analogy

With regard to the spent fuel analogy, the stability of the uraninite, both from hydrothermal effects during criticality (estimates range from 140° to 450°C at Oklo as compared to < 100°C in the SKB/TVO disposal concepts) and throughout geological time since then, is supported by the following conclusions summarised by *[Jakubick, 1986; Brookins, 1990]*:

- despite a high fission density, no trace of metamictisation of the uraninite was detected,
- the ^{239}Pu produced remained and decayed to ^{235}U in the uraninite matrix, and
- the fission products forming either metallic inclusions (Rh and Pd) in the host uraninite, or oxides stable in the uraninite structure (Th, Pu, REEs, Bi, Te, Y, and Nb), were retained within a few microns.

The analogy between spent fuel and Oklo uraninite is not, however, absolute; three important differences exist:

1) Oklo uraninite contains lower concentrations of fission products than spent fuel.

2) The maximum temperatures achieved at Oklo (up to 450°C) are lower than in a reactor and, consequently, the fission products in the Oklo uraninite will not have undergone fractionation to the same extent as spent fuel.

3) Oklo uraninite is better preserved than the UO_2 comprising the spent fuel rods because of a less complete nuclear reaction, thus rendering the reaction products less susceptible to groundwater attack.

Fission Product Mobilisation/Retention

Radionuclide transportation and retardation of the reaction products appears equivocal; the heavy actinide elements (noted above) were retained, as would be expected, but the lack of any movement may well be due more to the retention properties of the uraninite, than to insolubility and sorption from moving groundwater. More mobile radionuclides (^{90}Sr, ^{137}Cs, ^{99}Tc, ^{210}Pb) migrated away from the reaction zones, by relative amounts roughly in accordance with expectations of speciation/solubility, but not enough is known about the Eh, pH and temperature over 2 Ga to make possible a quantitative test of agreement and prediction.

Table 2.1 *[Brookins, 1984]* lists the elements of importance in the Oklo reactor zones and their evaluation in terms of retention and migration since criticality. More recent work in reactor 9 *[Curtis et al., 1989]* confirms the primary retention of Ru, Pd and Nd, the local retention of ^{99}Ru-^{99}Tc, and the migration and loss of Mo and Cd. In addition, Te, Ag and Sn, not quantified in Table 2.1, are described as retained, partially retained and lost, respectively. Studies of the retentive properties of the peripheral clay halo to reactor zone 9 *[Loss et al., 1989]* showed that considerable amounts of fissiogenic Mo, Ru, Pd, Ag and Te which escaped from the reactor zone, have been retained in the peripheral rocks, although Cd and Sn were not contained to any significant extent. ^{99}Tc and Sb indicated some retention.

Table 2.1: Element retention in the Oklo reaction zones (after *[Brookins, 1984]*).

Element	Comments	Eh-pH Predictions	
		25°C	200°C
Krypton	Most migrated	Not applicable	Not applicable
Rubidium	Probable local redistribution	Not applicable	Not applicable
Strontium	Probable local redistribution	Not applicable	Not applicable
Yttrium	Most retained	Retention	Retention
Zirconium	Most retained: some local redistribution	Retention	Some migration
Niobium	Most retained	Retention	Retention
Molybdenum	Most migrated	Migration	Migration
Technetium	Local redistribution	Retention	Migration (?)
Ruthenium	Local redistribution	Retention	Minor migration
Rhodium	Most retained	Retention	Retention
Palladium	Most retained	Retention	Retention
Silver	Most retained	Retention	Retention
Cadmium	Most migrated	Migration	Migration
Indium	Most retained	Retention	Retention
Tin	Not yet studied	Retention	Retention
Antimony	Not yet studied	Possible migration	Some migration
Tellurium	Not yet studied	Retention	Retention
Iodine	Most migrated	Not applicable	Not applicable
Xenon	Most migrated	Not applicable	Not applicable
Caesium	Most migrated (?: perhaps locally)	Not applicable	Not applicable
Barium	Local redistribution	Not applicable	Not applicable
REE	Most retained	Retention	Retention
Lead	Variable migration	Retention or local redistribution	Some migration
Bismuth	Most retained	" " "	Some migration
Polonium	Most retained	Retention	Retention
Thorium	Most retained	Retention	Retention
Uranium	Some local redistribution	Retention or local redistribution	Some migration
Neptunium	Most retained	Retention	Retention
Plutonium	Most retained	Retention	Retention
Americium	Not measurable	Retention	Retention

Although these data are merely qualitative, and much more detective work is necessary, such observational evidence is still a powerful means of convincing both the layman and the scientific community that fissionable products are largely retained in a natural environment which is somewhat analogous to that envisaged for a high-level spent fuel repository.

Radiolysis

An important factor in near-field safety performance assessment is the perturbation caused by radiation from the nuclear waste. Alpha radiolysis may mean that truly reducing conditions cannot persist around the spent fuel. The main radiation effect is the radiolysis of water, resulting in products such as hydrogen, hydrogen peroxide, oxygen etc. Modelling the net result of radiolysis assumed that all the hydrogen produced was effectively inert *[Neretnieks, 1982]*, and was subsequently lost from the system by diffusion, leaving an oxidising near-field.

The Oklo natural reactor was chosen as an analogue to such radiolytic effects for use in the KBS-3 repository safety analysis because of the high levels of radiation which have existed there over long periods of geological time. Two major aspects were addressed *[Curtis and Gancarz, 1983]*: 1) is there any evidence of an outward moving oxidation "front" from the reactor zone?, and 2) is there any evidence of element transport resulting from enhanced solubility due to the effects of the migrating oxidation front? Evidence was found to indicate that a net reduction to divalent iron, probably associated with a net increase in total iron, was associated with the reactor zone rocks; the aureole rocks showed less extreme reduction characteristics. The reduction of iron was considered mainly attributable to the hydrogen produced by the radiolysis of water during nuclear criticality. The addition of hydrogen, as the reduction mechanism, rather than the removal of oxygen, was favoured because the oxygen fugacity was considered much too low to facilitate oxygen removal.

In a comparison with the predicted radiation yields and rates of hydrogen for the proposed Swedish radioactive wastes, the calculated amount of radiolysis products/ton of spent fuel in one of the natural Oklo reactors *[Curtis and Gancarz, 1983]*, was found to compare favourably to the predicted case *[Christensen and Bjergbakke, 1982]*.

Present Analogue Status

The following general objectives have been listed for the present on-going studies at Oklo *[Blanc et al., 1988]*:

- methodology; what information can be obtained from the study of a natural analogue involving radioactive elements representing a range of mobilities in developing safety models for application to disposal sites?,
- evidence of significant phenomena for assessing radionuclide transfer during disposal in a deep geological formation, on "comparable" scales in terms of time and space,
- validation of specific models; long-term behaviour of rock materials offering similarities with that of clayey or bituminous engineered barriers or of schistic formations; migration into the geosphere (geochemical processes, thermal effects, irradiation effects), and
- general validation, by demonstrating that the models can simulate a real system, even though the site studied is different from that sought for waste disposal.

2.2.6 Palmottu

The Palmottu Analogue Project commenced in 1988 and the first phase of investigations were completed in 1992 *[Suksi et al., 1992]*. The project, earlier funded directly by the Finnish Ministry of Trade and Industry Energy Department (Publically Financed Nuclear Waste Management Research Programme), is now funded through the Finnish Centre for Radiation and Nuclear Safety (STUK). The project is operated as a cooperative effort between the Nuclear Waste Disposal Group of the Geological Survey of Finland, the Department of Radiochemistry at the University of Helsinki, the Laboratory of Engineering Geology and Geophysics at the Technical University of Helsinki and the Technical Research Centre of Finland (VTT).

The study concerns a small uranium mineralisation near Palmottu in south western Finland. One reason for setting up the study was that most international natural analogue studies concern sites with geological and hydrological conditions that differ substantially from those anticipated for a Finnish repository for nuclear waste.

The main technical objectives of the project include *[Blomqvist et al., 1991]*:

- characterisation of the structural and geohydrological conditions of the deposit area
- identification and quantification of the phenomena that have controlled the liberation of radionuclides from their primary minerals
- identification and quantification of the phenomena that have controlled the retardation of radionuclides in the rock-water system
- identification of the factors favouring the migration of radionuclides
- determination of the time-dependence of the processes identified
- assessment of the net migration of radionuclides

General Features

Geology/mineralogy

The Palmottu investigation site forms part of the supracrustal volcanic and sedimentary schist belt which continues across from central Sweden to SW Finland. The schist belt, which also forms a metallogenic province with numerous ore deposits, represents the Svecofennian domain of the Svecokarelian orogeny in which the main phase of plutonism and volcanism occurred 1.9-1.8 Ga. Associated with a late episode of granitic intrusion, the Palmottu uranium mineralisation (1.7-1.8 Ga) resulted from residual crystallisation fluids which explains why most of the U-Th minerals comprising the mineralisation are related to pegmatite and granite dykes.

Regionally the Palmottu site is located within a block feature bounded by distinct fault zones. Further subdivisions by a few prominent N-S trending fracture zones serve to control the groundwater flow in the area (Figure 2.14). The main rock type is a heterogeneous, garnet, hypersthene and often cordierite-bearing mica gneiss. The granites in the Palmottu area are mainly concordant with the schistosity of the enclosing gneisses. The dominant minerals are K-feldspar, quartz and biotite.

Fracture minerals include calcite (dominant), kaolinite, sulphides and Fe-oxyhydroxides; their distributions are dependent on the local groundwater flow patterns.

Uranium Mineralisation

The uranium mineralisation was discovered by airborne geophysical surveys in the late 1970s. This was followed up by the drilling of 62 prospecting holes (covering a maximum depth of 300 m) perpendicular to the regional deformation strike in order to intercept the mineralisation which is fracture controlled (Figs. 2.15; 2.16).

The deposit contains 1 million tons of ore with an average grade of 0.1% U. The orebody is discontinuous, with a total length of about 400 m extending partly under Lake Palmottu, and is 1 to 15 metres in thickness extending to around 300 m depth. Uranium occurs mainly as disseminations of uraninite, its alteration products (e.g. coffinite) and zircon; minor amounts of molybdenite are also in association. The uraninite is present in: a) coarse-grained feldspar-quartz-biotite pegmatites, and b) sheared granitic veins rich in quartz and biotite. Thorium is present as monazite.

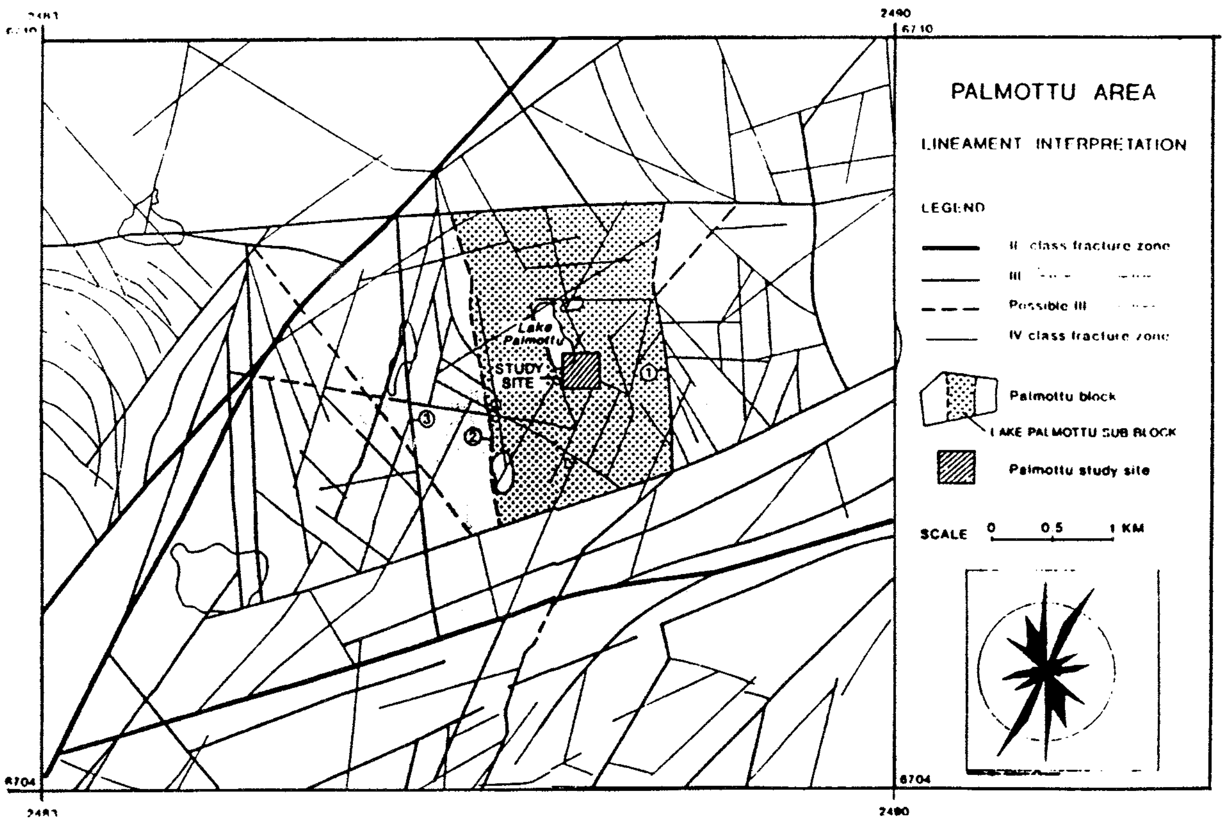

Figure 2.14 Lineament interpretation and block structures of the Palmottu area. The rose diagram shows the orientations of lineaments (from *[Blomqvist et al., 1991]*).

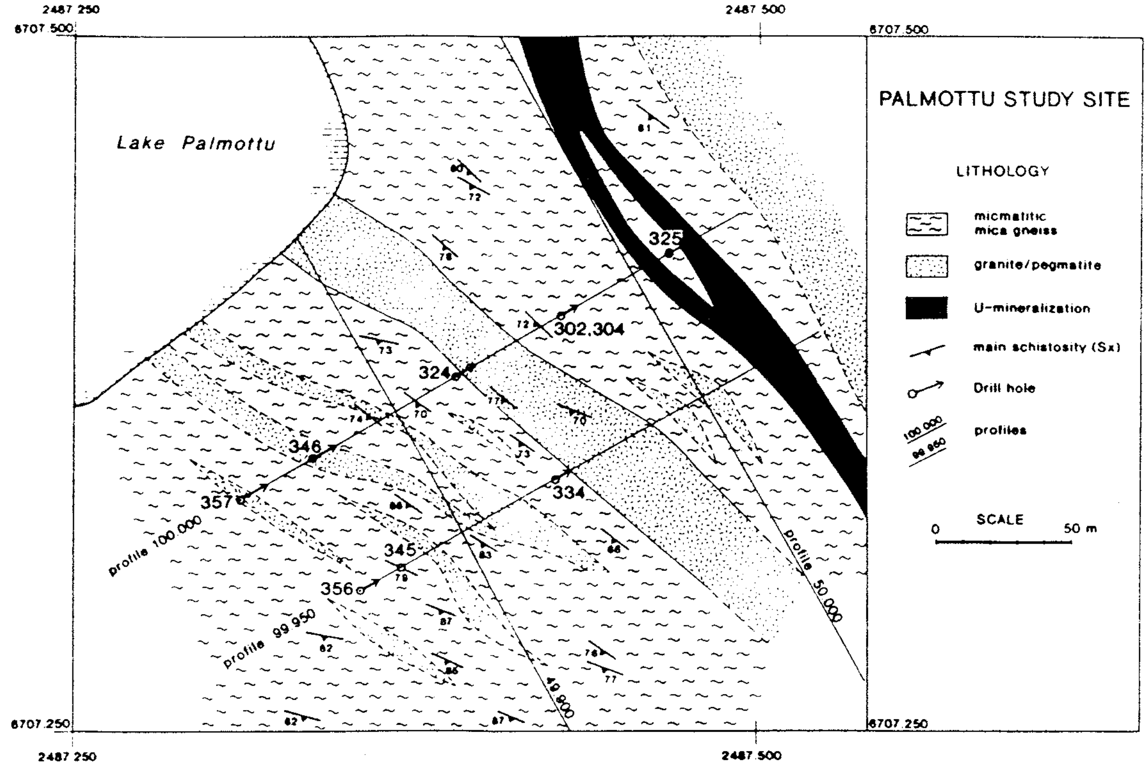

Figure 2.15 Lithological map and exploration borehole locations of the Palmottu U-Th deposit (from *[Kuivamäki et al., 1991]*).

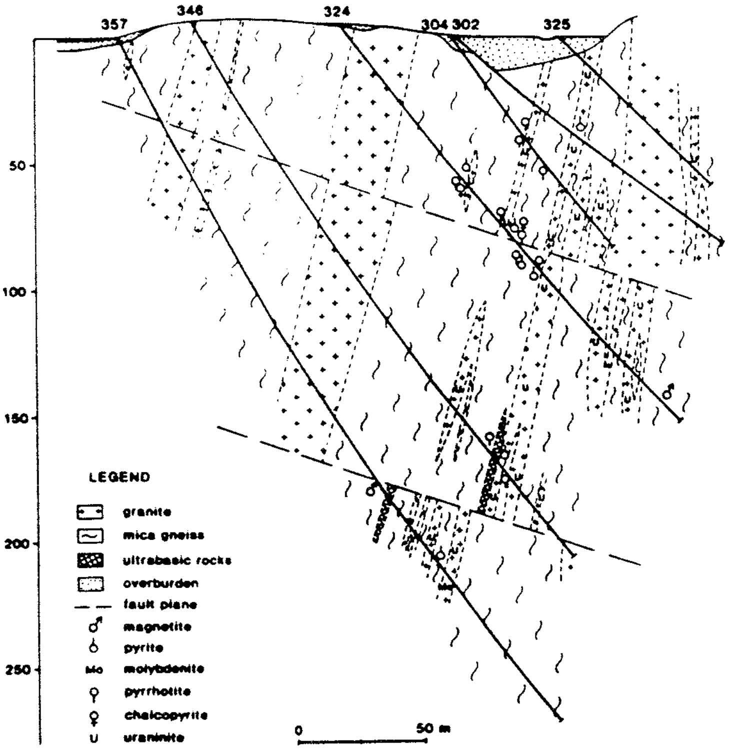

Figure 2.16 Vertical cross-section through the Palmottu U-Th mineralisation long one of the drillhole profiles (Profile 100 000; see Figure 2.15) (from *[Suksi et al., 1992]*).

Fracture studies indicate that a significant proportion of U in the rock is accessible, and that it is associated with easily dissolved minerals. The most efficient scavengers of U are the Fe-oxyhydroxides which are associated with altered plagioclase, biotite and calcite *[Suksi et al., 1991; Suksi and Tuominen, 1991]*. Calcite coatings on fracture surfaces also contain measurable amounts of U, which might indicate that U sorption/desorption processes may occur coevally with calcite formation. U-decay series measurements support radionuclide diffusion into the rock from the fracture zones; diffusion is limited to a narrow zone adjacent to the fracture surface.

In addition to U and its daughter isotopes, a suite of other elements were also measured. These included Na, Ca Al, Si (together with U) which showed enrichment in a 25 mm broad alteration zone adjacent to the fracture. Contrastingly, Fe, Sc, Co, S and Cu appear to have been immobile. Th, La and Sm exhibited similar behaviour to each other.

Hydrogeology

Conceptual models of groundwater flow through the Palmottu deposit are presently not available. Regional hydrogeologic evaluation and limited borehole hydraulic measurements have so-far been carried out *[Hakkarainen et al., 1991; Ahonen and Paananen, 1991]*. Regional studies have concentrated in producing a preliminary groundwater table map; the surface level of Palmottu lake appears to influence the general groundwater table. The groundwater table map will be used to determine the most significant underground water-flow directions and zones affecting the migration of radionuclides in and around the Palmottu uranium deposit.

The borehole measurements indicate that the hydraulic conductivities are higher in the upper bedrock than at greater depths; this can be related to an increased frequency of horizontal to sub-horizontal fractures towards the surface, a phenomenon very common to Fennoscandia due to stress-release following glacial retreat. Some of these fractures are water conducting (often granitic veins or their contacts with the mica schist) and some also intersect the mineralisation. At the moment the full scale of hydraulic connection is not known.

Hydrogeochemistry

The groundwater chemistry and redox conditions have been determined from several of the boreholes; sampling both from open-holes and packed-off borehole sections has been carried out *[Blomqvist et al., 1992]*. The groundwater chemistry ranges from dilute Ca-HCO_3 waters to dilute Na-Ca-HCO_3-SO_4 waters, representing a evolutionary trend from recharge surface water high in tritium to deeper slightly SO_4-dominated saline waters low in tritium associated with uranium-bearing (+ sulphide) horizons. Mixing of these two main groundwater types occurs along interfaces between different fracture controlled aquifers, and in the upper part of the bedrock where, depending upon local small-scale hydrology, either dilute surface waters recharge or deeper groundwaters discharge.

As expected, changes in dissolved uranium concentrations correlate with changes in redox potential which in turn reflect variations in depth. The solubility-limiting solid phases for uranium and thorium appear to be uraninite and thorianite respectively. A clear discrepancy was noted between measured and calculated Eh-values when equilibration of groundwater and pyrite was assumed *[Ahonen et al., 1992a]*. The calculations show that the stability field of pyrite is expanded towards higher redox potentials in the presence of metastable soluble sulphoxy anions. There are also indications that the $Fe_{(II)}/Fe_{(III)}$ redox couple may play an important role.

Colloids

Preliminary data confirm the presence of colloidal material of different types in the groundwaters. At depth, the colloids (1-500 nm in size) are generally inorganic in composition containing Si, K, Ca and Al with minor amounts of S, Na and Fe. The presence of minerals such as plagioclase, K-feldspar, mica and quartz was also confirmed. Close to the mineralisation Fe-containing colloids were observed which may be Fe-oxides or Fe-compounds of organic origin. Both U and Th are associated with the colloidal fraction. Studies are in progress.

The Natural Analogue

As a potential analogue site, Palmottu was chosen for the following reasons *[Blomqvist et al., 1991]*:

1. The Palmottu deposit is situated in an area of crystalline bedrock that in certain important features is similar to the areas which are being studied as possible sites for the future repository of high-level radioactive wastes in Finland.

2. The mineralising phases comprising the Palmottu deposit are Precambrian in age and relate to the Svecokarelian orogeny; the uranium and thorium in the deposit thus represent tracers that may indicate the amount and extent of radionuclide migration since 1.8 Ga ago.

3. The area belongs to the Fennoscandian Shield which has undergone several glaciations during the last million years during which substantial isostatic adjustment has fractured the bedrock. Such vertical movements, together with climatic change, also involves changes in groundwater flow and chemistry which may be repeated in connection with future glaciations. Such phenomena, critical for any waste disposal scenarios in Finland, may be studied comprehensively at Palmottu.

4. At Palmottu, overlying the deposit,there are postglacial layers of organogenic sediments (peat and mud) that may record migration and retention of radionuclides during the last less than 10 000 a.

In terms of direct application to repository performance assessment, the following two major aspects have been considered *[Smellie, 1991]*:

- Near-field spent fuel solubility/dissolution
  - geochemical modelling of ore dissolution (uranium solubility/speciation).
  - geochemical modelling of additional trace elements present in solution considered important in safety disposal (e.g. Th, Tc, Pu, Cu, Mo, As, Cs, Sr etc.).

- Far-field Radionuclide Mobilisation/Transportation.
  - the effects of groundwater redox chemistry on the dissolution and transportation of radionuclides (and other trace elements)
  - the role of colloid/organic material on the uptake and transportation of radionuclides
  - the role of microbes on the groundwater redox chemistry
  - the role of fracture mineralogy (e.g. $Fe_{(II)}$-bearing phases) on the groundwater redox chemistry
  - the role of fracture mineralogy on radionuclide mobility (e.g. sorption processes)

- the role of matrix diffusion in the uptake of radionuclides

2.2.7 Other analogue studies

Broubster

The Broubster site is located about 16 kilometres south west of Thurso in northern Scotland (Figure 2.17). Anomalously high concentrations of uranium have been found in peat-rich deposits at the site. This anomaly (estimated total of 600 kg U; mean concentration of 400 ppm U) has been investigated in detail as a part of the radioactive waste disposal research programme carried out by Her Majesty's Inspectorate of Pollution.

The current understanding of the mechanisms behind the development of the anomaly has been summarised in *[Read et al., 1991]*. The region where the anomaly occurs is flat and marshy. The peat-rich top layers are underlain by cyclic deposits of Devonian sedimentary rocks which rest on the much older metamorphic basement. The Devonian bedrock comprises a sequence of grey micaceous sandstones, siltstones, black shaley mudstones and finely laminated limestones. The contents of uranium and thorium are usually low in the sandstones whereas the shales and limestones may contain in excess of 20 ppm U. The limestone is cut by a significant north east trending fault bringing up massive calcareous sandstone; where the carbonate cement (calcite, dolomite, ankerite) is intact, it can contain more than 100 ppm U. Where the sandstone has been decalcified the uranium content is less than 30 ppm. From these observations the sandstone in the fault zone is considered to be the main uranium source feeding into the anomaly in the superficial peat layers.

The highly permeable fault, which forms the main drainage access within the site, has been found to respond rapidly to rainfall and substantial upwelling has resulted from heavy rains. The water percolates into the rock down to 15-20 m depth in the western part of the area and emerges in the eastern part. A schematic diagram of the flow system is illustrated in Figure 2.18 together with the identified main sources and sinks for uranium.

Peaty organic matter is the predominant near-surface sink for the uranium at Broubster. A volumetrically less important sink is associated with manganese oxides which lie directly above the decalcified sandstones.

The postulated scenario is that uranium (source term) contained in the sandstone has been oxidised and removed as carbonate complexes and fixed and concentrated in post-glacial peat. There is also evidence that some uranium has been associated with precipitated iron and manganese oxides and re-immobilised. It considered likely that the present-day situation is the result of multiple leaching and retention processes due to periodic changes in the groundwater table.

All waters at Broubster are oxidising (Eh 200-400 mV) and slightly acidic (pH 5.3-6.7). The uranium found in the groundwaters is predominantly as organic complexes, mostly with fulvic acids as ligands. These complexes occur in "true" solution (particle size <2 nm). Model studies have shown that the fulvate complexes compete successfully with other possible species at pH below 7.5 which should be compared with the pH around 6 measured at the site. It has been concluded that the uranium leached migrates from the source location in the form of uranyl fulvate complexes.

The enrichment of uranium in the peat is substantial, the peat/water concentration ratio being about 10^5 in the centre of the anomaly. Column experiments have shown that the peat has saturation limit of about 16 % by weight with respect to uranium. As the concentrations measured are only about 1/100 of this value, it can thus be concluded that the peat has not yet been saturated but will continue to retain uranium.

Uranium in the peat is predominantly associated with organic matter. Column experiments and uranium decay series measurements indicate that the uranium in the peat is in equilibrium with uranium concentrations in the water. The main mechanism for the binding of the uranium to the peat is believed to be complexation, presumably bound to carboxylic groups on the humic substances in the peat. This binding is observed to be very strong and probably accounts for the quoted high peat/water concentration ratio and also explains why so little of the uranium has migrated into other soils adjacent to the peat.

The Natural Analogue.

At Broubster, the U anomaly in the peat is known to have formed over the last 5 000 a since the last glaciation. It thus represents the end result of mobilisation and from mineralisation present in the Devonian sandstone and subsequent groundwater transport over a distance of 100-200 m to the peat accumulations. The main objective of the study was to increase the understanding of migration behaviour (processes, rates and distributions) of radionuclides and elements in a specific well constrained environment, and to use these physical and chemical boundary conditions to improve confidence in modelling uranium speciation and mass transport of different elements using performance assessment related computer codes and thermodynamic databases *[Hooker et al., 1992]*.

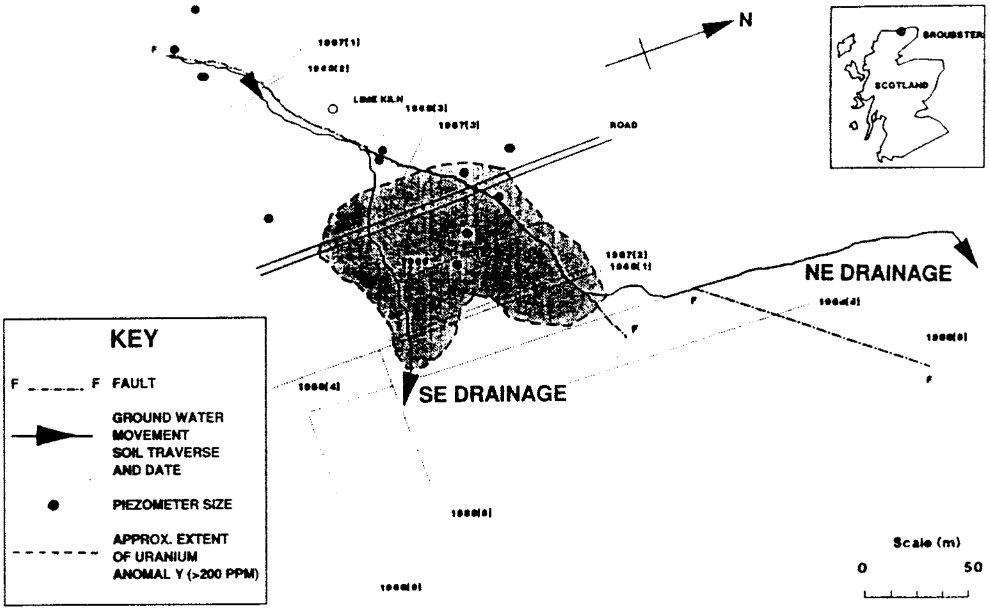

Figure 2.17 The Broubster natural analogue site (from *[Read et al., 1991]*)

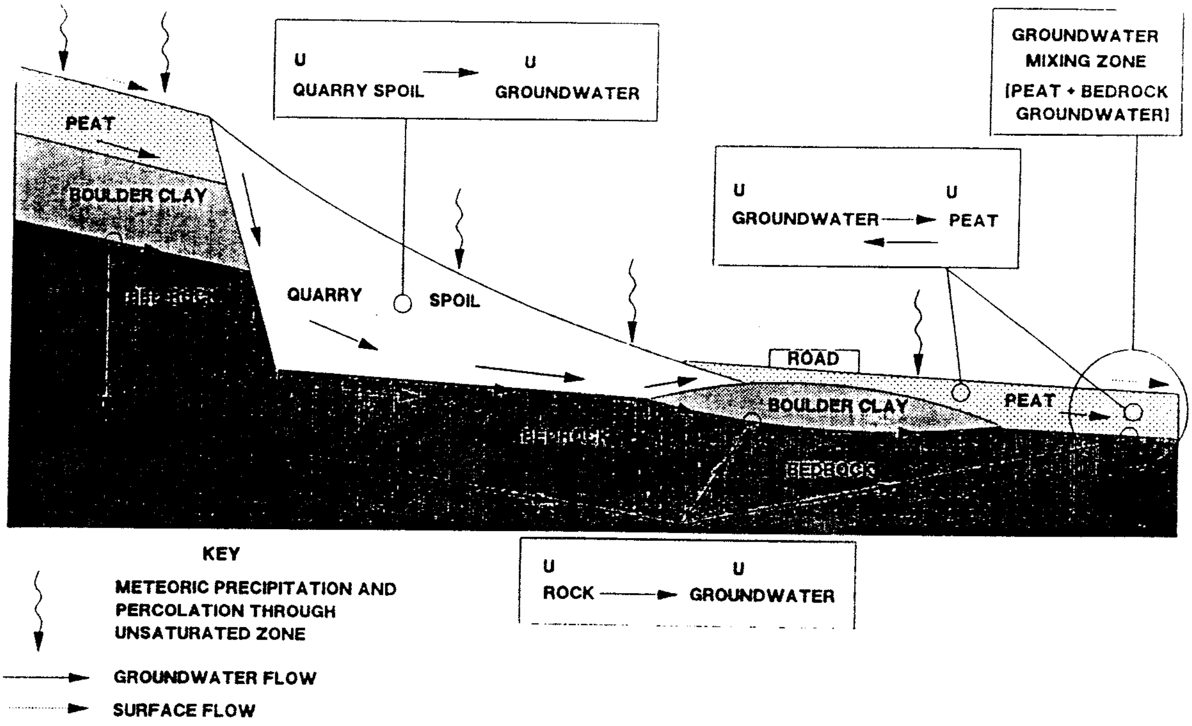

Figure 2.18 Schematic view of the groundwater flow system at Broubster. The areas of dissolution and immobilisation of uranium are also indicated (from *[Read et al., 1991]*).

Needle's Eye

The Needle's Eye natural analogue site, which has been under investigation since 1986, is jointly funded by Her Majesty's Inspectorate of Pollution (U.K. Department of the Environment) and the Commission of the European Communities (CEC). The study has been designed to provide data enable validation of thermodynamic speciation models and coupled chemical transport codes.

The site is located on the north shore of the Solway Firth in southwest Scotland (Figs. 2.19; 2.20). Here uranium is present as several veins of predominantly pitchblende (UO_2) associated with secondary minerals such as uranophane (Ca-U silicate). The mineralisation is located along faults trending north beneath coastal sediments and then outcropping in a cliff comprising an intrusive granodiorite formation in Palaeozoic metasedimentary rocks of Silurian age *[Roberts et al., 1989]*. The uranium mineralisations are partly exposed to the atmosphere leading to the dissolution of hexavalent uranium which migrates with superficial groundwater to a silty sediments whereupon it is fixed by sorption mainly onto humic substances and ferric oxyhydroxide. At least one of the mineral veins extends under the sediments.

Investigations at the site have included sampling of sediments and water as well as hydrogeological studies carried out using plastic tubes and piezometers emplaced in the sediments. Furthermore, the lithological, hydrological and geochemical profiles of the sediments have been studied in a 1.8 m deep pit dug into the sediments about 20 m from the cliff (Figure 2.20). Based on the measured distribution of hydraulic head, uranium activity ratios of the natural decay series radioisotopes and the recorded profiles in the pit, a conceptual model of the groundwater flow and uranium migration has been constructed (Figure 2.21). Essentially, at the foot of the cliff there is a strong sub-vertical component driving groundwaters containing dissolved uranium upward through the sediments. The groundwater flow system has been modelled using the finite-element technique *[Noy, 1990]*.

Data from the investigations at Needle's Eye have been used in the modelling of couple chemical transport *[Jamet et.al., 1990]* and also with chemical speciation models *[Doublet et al., 1989]*.

The Natural Analogue.

The main aim, in common with the Broubster analogue study, was to identify an occurrence of uranium mineralisation which acts as a source of radionuclide mobilisation for subsequent transport through sediments. Knowing the source term, the transport paths and the solubility and speciation of uranium, provides a basis to test coupled chemical transport codes and databases used in performance assessment.

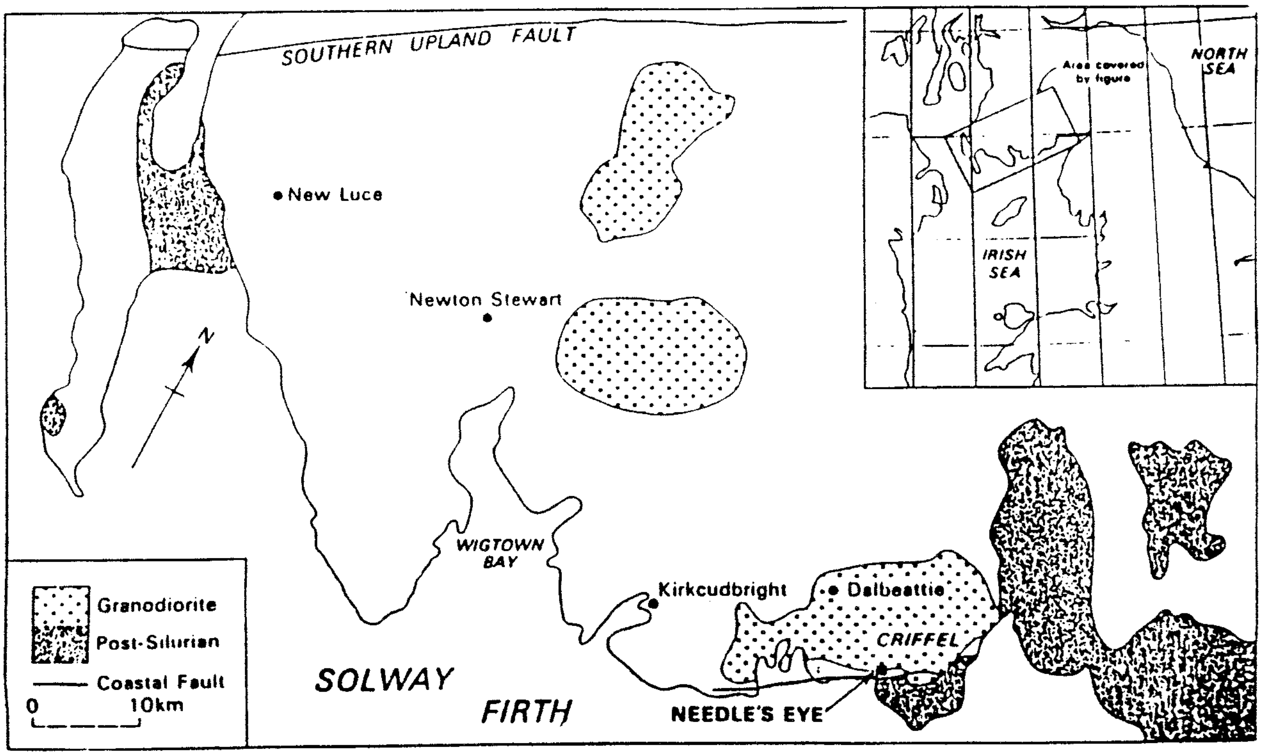

Figure 2.19 Location of the Needle's Eye natural analogue site. (From *[MacKenzie et al., 1991]*)

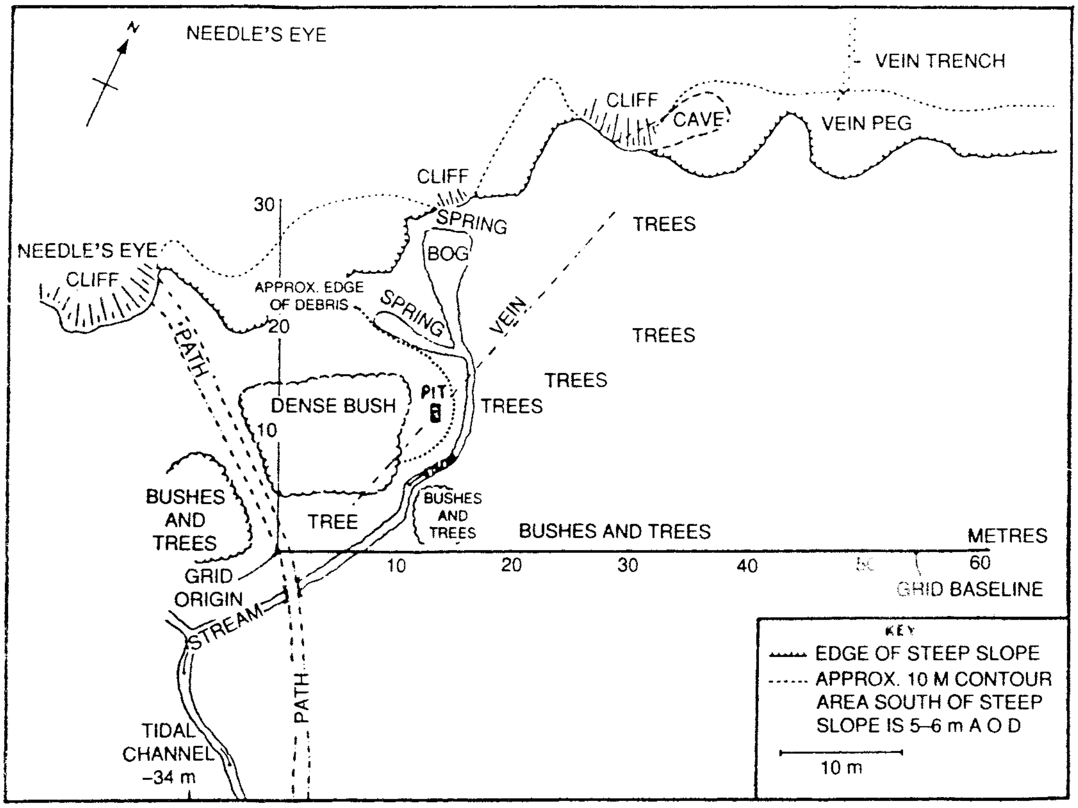

Figure 2.20 Main features of the Needle's Eye natural analogue site. (From *[Roberts et al. 1989]*)

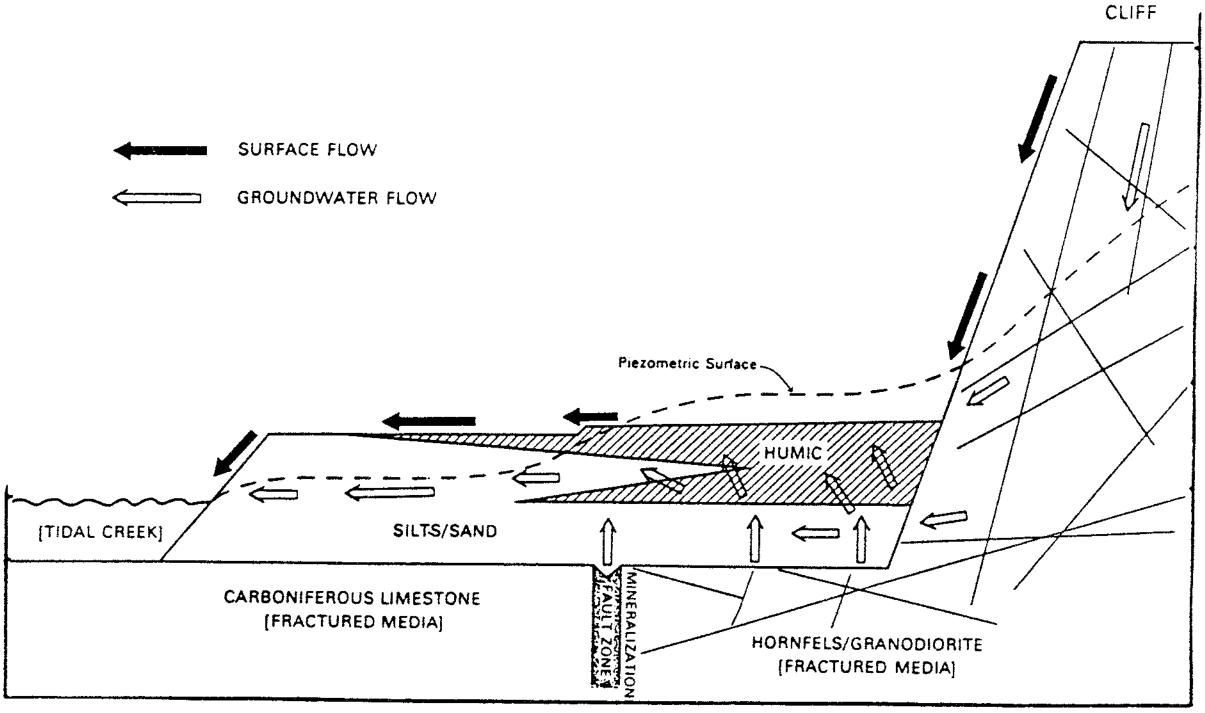

Figure 2.21 Conceptual model of the water flow regime at the Needle's Eye natural analogue site. (From *[Roberts et al. 1989]*)

Oman

The high alkaline spring waters in Oman in the Arabian Gulf were studied as an analogue for the near-field of a nuclear waste repository containing large volumes of cement and concrete; reaction of groundwaters is expected to result in a highly alkaline and probably reducing chemical environment. The project was funded jointly by UK Nirex Ltd. and Swiss National Cooperative for Radioactive Waste Management (Nagra), and was completed in 1987 *[Bath et al., 1987]*.

The hyperalkaline, calcium hydroxide rich artesian springs of Northern Oman are found in association with the Semail Ophiolite Nappe (Figure 2.22). Deposits of $Ca(OH)_2$ and $Mg(OH)_2$ and other anomalous minerals occur at the points of groundwater discharge. The waters range from pH 10-12, tend to be saline and are often extremely reducing and contain free hydrogen gas. The hyperalkaline water is thought to be the result of weathering of the ophiolitic ultramafic rocks (i.e. low temperature serpentinisation reactions) which are low in silica content and high in magnesium and iron.

The site investigations comprised the sampling of spring waters at seven localities; measurements of pH, Eh, alkalinity and temperature were carried out in situ, with subsequent laboratory determinations of major and trace elements. Separate samples were also collected for microbial analyses. Extensive use was made of published hydrochemical and mineralogical data from previous studies *[Neal and Stanger, 1983, 1984a-b, 1985]*.

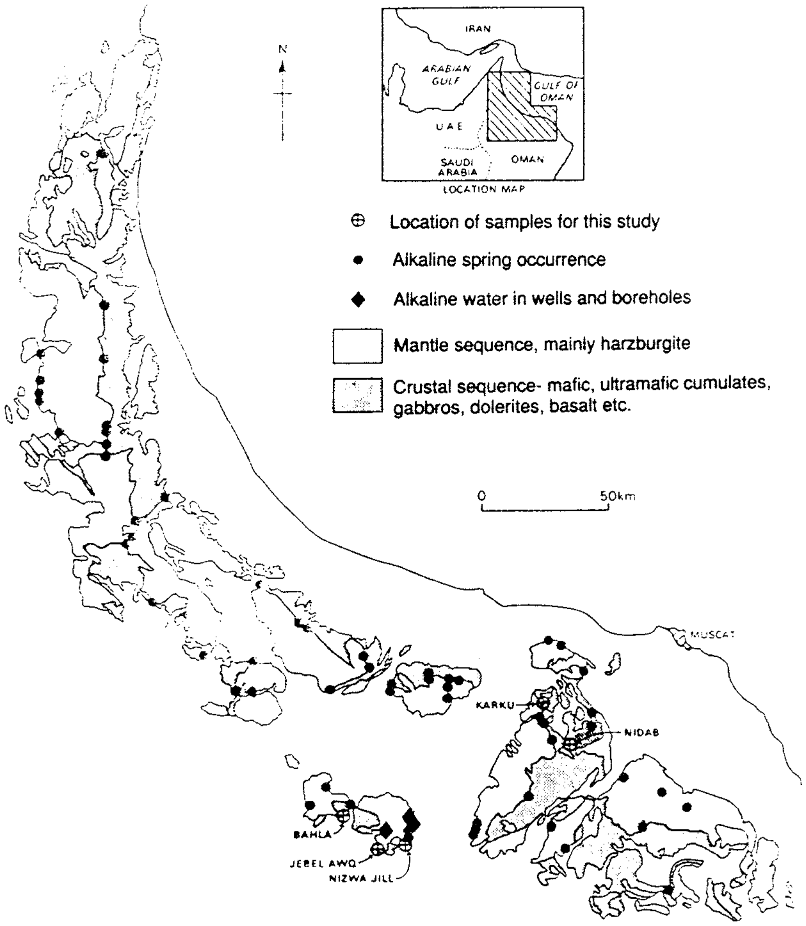

Figure 2.22 **Hyperalkaline springs and sampling locations along the Semail Ophiolitic Nappe, Northern Oman (from *[Bath et al., 1987]*)**

The Natural Analogue.

Important analogue issues of the study were:

- to increase the understanding of processes in and around a radioactive waste repository exposed to high-alkaline conditions over extended time-scales
- to study the reducing conditions established by the formation of Fe(II) compounds and hydrogen gas
- to study the solubility and speciation of a number of trace elements of potential interest for radioactive waste repositories
- to study the presence and role of microbes in an alkaline environment.

Maqarin

The highly alkaline springs of the Maqarin area of NW Jordan (Figure 2.23; 2.24) are currently being investigated as part of an international project testing models used in the performance assessment of low- to intermediate-level radioactive waste repositories. The Maqarin area provides a rock-groundwater system which is an ideal natural analogue of a cementitious repository in a sedimentary host rock *[Alexander et al., 1992]*. The project commenced in 1990 jointly funded by the Swiss National Cooperative for Radioactive Waste Management (Nagra), Ontario Hydro and UK Nirex Ltd.; more recently (1991) the Swedish Nuclear Fuel and Waste Management Co. (SKB) became involved.

Geologically, the site area comprises late Cretaceous marls and bituminous limestones (i.e. Bituminous Marl Formation) overlain by Tertiary chalks and limestones followed by Pleistocene alkali basalts (no longer present at Maqarin) and Recent sediments forming poorly sorted slope wash and wadi fill materials and residual soil. Travertines, stalactites and stalagmites are common around springs and seepages *[Khoury et al., 1992]*. The bituminous rocks are biomicrites (calcite + quartz, dolomite, apatite pyrite and clays such as illite, kaolinite and illite/smectite mixed layers) with organic contents between 15-20% and SO_3 up to 12%; trace elements (including U) are mostly adsorbed by the organic material. The organic material is not bitumen, but probably more akin to kerogen.

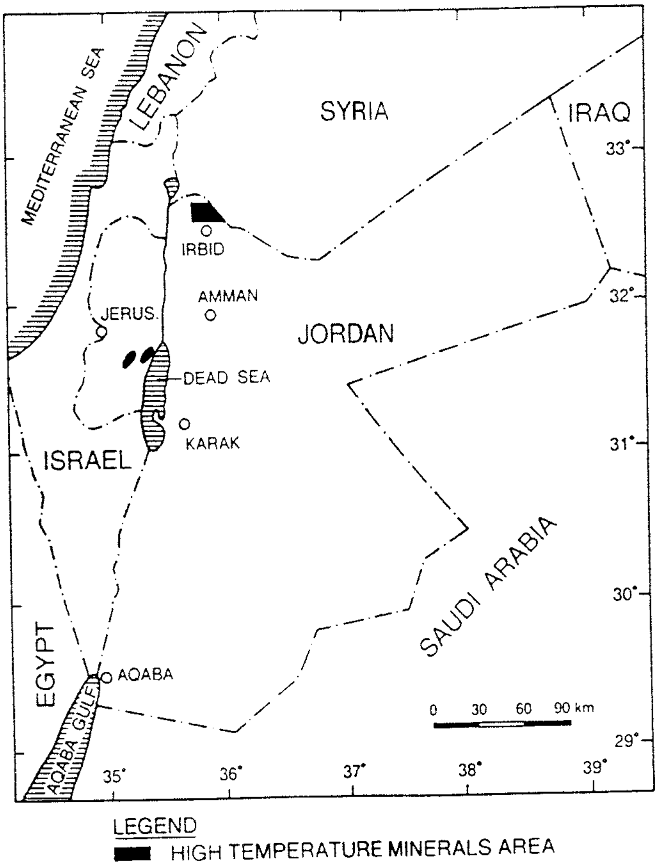

Figure 2.23 Location of hyperalkaline groundwaters at Maqarin, NW Jordan (from *[Khoury et al., 1992]*)

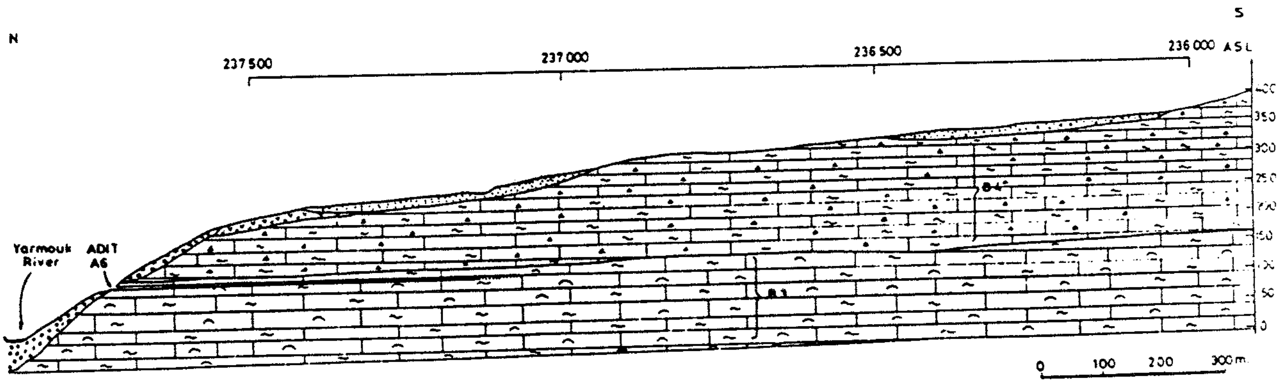

Figure 2.24 Schematic N-S geological cross-section through the Maqarin site area showing the extensively sampled Adit A6 and its position relative to the Yarmouk river (from *[Khoury et al., 1992]*).

The Bituminous Marls have commonly undergone spontaneous combustion (> 1000°C) resulting in widespread thermal metamorphic reactions. The chemistry of the hyperalkaline groundwaters (up to pH 12.5) results from the interaction of normal aquifer waters (pH 7-8) with these thermally metamorphosed marls. Subsequent hydration of this high temperature mineral assemblage formed portlandite, ettringite, thaumasite and numerous other cement minerals *[Khoury et al., 1992]*.

Groundwater and rock samples have been collected from an exploration adit and from various seepage localities. Natural springs in the near-vicinity of the Maqarin area have also been sampled to establish the input source groundwater term. In situ measurements of pH, Eh and temperature were made and subsequent analysis of major and trace element ions and environmental isotopes. Regarding trace element studies, the main focus has been on U, Th, Ra, Se, Pb, Ni, Se and Sn. Samples for microbial and organic material studies were also taken.

The main objective of the study has been to make blind calculations of trace element solubilities (i.e. by calculating saturation indices at an assumed solute concentration of $1 \bullet 10^{-6}$ g/l) and speciation in the alkaline waters, and subsequently to compare the results of the various modelling teams by employing different models and thermodynamic data bases normally used in performance assessment *[Alexander et al., 1992]*.

The Natural Analogue.

There are some similarities in the analogue approach between Maqarin and Oman. However, there is one main improvement: at Maqarin the high pH of the groundwaters is a product of interaction with naturally occurring cementitious minerals, and not by the alteration of ultramafic minerals as is observed in the ophiolites of Oman. One disadvantage is that the groundwaters so far sampled at Maqarin are oxidising.

3. Geochemistry

3.1 General

The geochemstry in the groundwater and in the repository host rock influences the performance and the safety in several ways. For example, the groundwater chemistry has an impact on the durability of canister materials, the solubility of the waste constituents and on the speciation of radionuclides dissolved in the groundwater. Moreover, the mineral composition of the rock surfaces in contact with the groundwater is essential for the amount of retention by sorption or other interactions that the radionuclides undergo.

There are several computer codes available for the modelling of geochemical equilibria. These codes are typically associated with data bases containing thermodynamic data or equilibrium constants for the reactions that can be anticipated to occur in the groundwater/mineral system. The quality and completeness of the data in the data base is of course crucial for the success the modelling. The studies of natural analogues offer opportunities to test both data bases and computer codes. This is done both by using the models to simulate the observed geochemistry at the analogue site as part of the interpretation of the site features, and by attempting to predict the geochemical characteristics of the system by combining independently collected thermodynamic data with concentrations of major species measured at the site in model calculations of chemical parameters and subsequent comparison with corresponding measurements from the site. The purpose of such a prediction is to try to validate the geochemical site model including the thermodynamic data base. A review of different simulation and prediction exercises is given below.

The redox conditions in the repository and along the flow paths are of particular interest as the solubility and sorption tendency of many radionuclides depend on the oxidation state they are in. Below a simple model that relates the redox conditions to the equilibrium between ferrous and ferric iron is tested by applying the model to data from a number of natural analogue studies and site investigations.

3.2 Testing of geochemical models

3.2.1 Geochemical modelling exercises

Poços de Caldas

The solubility and speciation of trace elements from spent fuel and high-level waste from reprocessing under varying redox conditions is important in virtually all design concepts for the near field hitherto considered. One of the four overall objectives of the Poços de Caldas project has been "to assist in the validation of hydrogeochemical equilibrium thermodynamic models, codes and data bases which are used to evaluate rock/water interactions and the solubilities and speciations of elements, using information from environments rich in REEs and natural series radionuclides" *[Smellie et al., 1988]*. This was done by in two phases *[Bruno et al., 1991]*. In the first phase four groups were provided with the major element chemistry of water samples from the Morro do Ferro boreholes MF10, MF11 and MF12. In order mainly to compare the data bases used, each group was asked to predict the solubility-limiting phase, the saturation concentration and the aqueous speciation at saturation for U, Th, Pb, V, Ni, Sn, Se and Ra in each of these waters. In the second phase five modelling groups were provided with major component composition and master-variable values for three selected waters from the Osamu Utsumi mine and Morro do Ferro. The task given to the groups was then to predict the solubility limiting phases, the total concentration in the groundwater and the speciation of some specified trace elements (U, Th, Pb, Sr, Ni, Mn, Al and Zn).

It was concluded from the first phase that calculations from the various groups were in satisfactory agreement (within one logarithmic unit in trace element concentration) with the exception for uranium where differences in U(IV) hydrolysis caused greater differences *[Bruno et al., 1991]*. The model predictions generally gave higher solubilities than the analyses from the site. It was argued that the solubility could be controlled by more than one phase and that, for example, coprecipitation with ferric oxyhydroxides may be of importance.

The results of the predictions in the second phase were reasonably consistent with field observations. The model predictions were generally conservative (higher saturation concentrations than measured). For Zn and Ni, however, one team underpredicted the saturation concentrations assuming that ferrite minerals were solubility controlling. It was recommended on the basis that they are unlikely to form under low-temperature conditions that ferrite minerals should be excluded from solubility limit calculations unless there is evidence that they are formed at the site investigated.

The reasons for overpredicting the solubilities are probably somewhat different for different elements. For Th overpredictions occur when phosphate complexes are included. This could be due either to exaggerated phosphate analyses (measured value on or below detection limit) or overestimated stability constants. For V the low field analyses could be due to source-term limitations while it may reflect that essential minerals are missing in the data bases. In the case of Ni, Zn and Mn the solubility may be limited by coprecipitation with ferric oxyhydroxides.

The extent of agreement between predictions of the speciation was variable. For example for Sr, Ni, Zn, Al and Mn it was very good while it was poor for U and Th. The predicted speciation could be compared to some extent with results from ion-exchange/colloid fractionation. The predicted speciation was reasonably consistent with the experimental data for Al and Mn and, in some cases, U and Th. It was concluded that further development of speciation analysis techniques would be of value due to the great importance of sorption in performance assessments.

Oman

In several repository concepts for disposal of low- and intermediate level radioactive waste, cement is used as solidifying agent and in structural barriers in the repository. The solubility and mobility of radionuclides in the alkaline and often reducing environment in such a repository are thus of central importance for the repository performance. Models of equilibrium chemical thermodynamics constitute a potentially valuable tool for evaluating the elemental solubilities and speciations. The applicability of thermodynamic modelling is, however, limited by the availability of relevant data. A further limitation of the applicability of the modelling is that most data to be input to the models have been derived in the laboratory under acidic to neutral pH-conditions, and that only few laboratory data from strictly reducing conditions are available. Examination of the highly alkaline and reducing groundwaters at Oman is complementary to laboratory investigations as *i)* the chemical environment (high pH, very reducing) is difficult to simulate in the laboratory and is readily disturbed (e.g. by contamination of small amounts of CO_2 or O_2), and *ii)* the reaction times in the natural system may be long enough to place the system closer to equilibrium than would possible in the laboratory.

Model predictions of trace element solubilities and speciation in the Oman groundwaters have been modelled *[Bath et al., 1987]*. The behaviour of the fission/activation products Se, Pd, Sn, Zr and Ni were modelled using a thermodynamic data base compiled by the Paul Scherrer Institute. Due to uncertainties in the data base and in the observed lack of equilibrium in of the sulphur system in the natural waters, the sulphidic species were not included in the base calculations. The actinides, Th and U, were modelled using an extended MINEQL data base.

A particular difficulty in comparing predicted and measured elemental concentrations in the Oman study was that the concentrations of the trace elements of interest were generally below the detection limits for state-of-the-art analytical methods. This was concluded to depend on a combination of the high pH depressing the solubilities and a possible lack of mineral source for some of the elements. The model predictions for Se, Zr, Ni, Th and U solubilities were, however, within or close to the detection limits. With the exception of Pd the models predict higher solubilities than the measured. For Pd it is commented *[Bath et al., 1987]* that the measurements might be too high due to interference with Sr on the ICP-MS peak. It is therefore identified that more experimental work is needed to confirm the low model predictions of the Pd solubility. Also Ni is suspected to be subject to analytical errors due to contamination of samples from the analytical equipment.

For Se and Zr no obvious source for the trace elements is found in the minerals on the site. It is therefore possible that the low concentrations observed reflect a source limitation. The predicted concentrations of Sn are very low. This could be regarded as consistent with the analyses that are below the detection limit.

The measured uranium concentrations are below the calculated for samples. In particular the concentrations for oxidising conditions are low. This could either be an artefact of air contaminating originally reducing samples, or it might indicate that solid phases of hexavalent uranium such as $Ca(OH)_2 \bullet UO_2(OH)_2$ are present.

No quantitative semi-quantitative validation of the models were obtained in the Oman exercise. The study did, however, highlight the problems involved in using very low concentrations for model validation purposes. The study also shed light on some sensitive areas of the modelling of the particular elements studied. It was concluded that the studies of the extreme, and for the concrete barriers relevant, chemical environments of Oman should be complemented with similar studies on more normal groundwaters with better known trace element sources and buffering reactions.

Maqarin

For the Maquarin natural analogue site "blind" predictions of trace elements have been performed for three typical high-pH (approx. 12.5) groundwaters *[Alexander et al., 1992]*. These predictions will later be compared with actual analyses from the site. Four groups participated in the exercise using different data bases and computer codes. The scope of the calculations was limited to calculating the aqueous speciation of seven trace elements (U, Th, Ra, Se, Pb, Ni, and Sn) each having a total concentration of $1 \bullet 10^{-6}$ g/L and to estimating the saturation with respect to possible solubility-limiting phases. There was thus no attempt to equilibrate the groundwater with the solid phases.

The solution chemistry provided to the modelling groups was not charge balanced. One of the groups did balance the charge by reducing the hydroxide concentration for one of the three waters thus lowering the pH from 12.5 to 12.2.

An important conclusion from the exercise was that the different computer codes behaved very similar, and that the differences between the results of the different groups could be attributed to differences in the data bases employed. Differences occur in the databases when there is either a lack of data or when the data-base compiler has made subjective choices between varying literature data.

Since the Maquarin geochemical modelling exercise has been carried out "blindly", i.e. without access to analyses on the trace elements, and since no comparison with actual analyses has yet been made, nothing can be said about the correctness of any of the modelling results. Nor can anything be stated about the validity of the models. It is obvious, however, that the results of the modelling are valuable guidance for the ongoing chemical analyses at the site. For example, the modelling groups pointed out the importance of investigating major Ni, Se and Sn phases in the rock in the Maquarin area. They also showed that spending much effort on finding the exact solid uranium phases is of little utility as there is still much debate about the solution chemistry of uranium.

Cigar Lake

Within the Cigar Lake Project a prediction of trace element concentrations was made based on analyses of major component concentrations and master variables *[Casas and Bruno, 1992]*. The predicted trace element concentrations were then compared with measurements from the site for the elements for which such measurements were available. The modelling methodology included three steps; *i)* establish the solubility-limiting solid phase, *ii)* calculate the total trace-element concentrations with the selected solubility-limiting phase, and *iii)* determine the speciation of the trace elements in equilibrium with the solubility limiting phase. The trace elements modelled were U, Pu, Th, Tc, Cu, Ni, Ba, Pb, Sr, Zn, Mo, Cr and As.

The predictions were reasonably in agreement with the field observations for those elements for which the data base contained good quality data (Ba, Cu, Th and to some extent Zn). This is concluded to indicate that the equilibrium approach gives a reasonable description of the natural system.

For Ni and Pb most of the measured groundwater concentrations are below the detection limit and thus too low to allow a direct comparison with the calculations. Both the calculations and the mineralogical characterisation indicate that the sulphides of Ni and Pb are formed in the ore zone yielding a too low solubility to be measured. For half the few analyses that are above the detection limit the calculated and measured concentrations agree well whereas the model predictions are highly non-conservative.

The elements that were not well predicted in the modelling can be divided into two groups. The first group, consisting of Sr, As and Mo, was conservatively modelled, i.e. the predicted concentrations were higher than the measured. A likely reason is that the data base did not contain key minerals for these elements. The second group which was non-conservatively predicted contained Cr. A possible reason could be that there is no solubility-limiting solid phase present at Cigar Lake. It should be noted, however, that only two reference groundwaters have Cr concentrations above the detection limit.

Other analogue studies

At Broubster *[Read and Hooker, 1989]* and at Needle's eye *[Doublet et al., 1988]* Geochemical modelling has been used to interpret the uranium chemistry at the respective site. Neither of these exercises have had the ambition to be model validation exercises. They have, however, been valuable tools in the interpretation of the site hydrogeochemistry and formed bases for the subsequent transport modelling.

The modelling at Broubster has shown that the predominant oxidation state is U(VI) at the site. The concentrations of uranium are not solubility controlled as the waters are calculated to be undersaturated with respect to the common uranium minerals uraninite, coffinite and rutherfordine. The predominant uranium species in solution is uranyl carbonate. At lower pH humic acids compete successfully with carbonates at lower pH. The breakpoint varies between pH 6 and pH 7.5 depending on the data base used.

The Needle's Eye modelling was carried out with the objective to interpret the sources and transport paths for uranium at the site. The calculated saturation indices for various minerals have been an important tool in this interpretation process.

Efforts to interpret the geochemistry of the weathering processes at the Koongarra uranium mineralisation have been carried out within the Alligator Rivers Analogue project *[Duerden (Ed.), 1992a]*. In particular, the modelling has aimed at investigating the mechanisms for the formation of solid phases of hexavalent uranium, specifically uranyl phosphate and uranyl silicate. This is reviewed in Chapter 4.

A disused uranium mine at South Terras, Cornwall, has been studied with uranium concentrations in stream waters passing the mining spoils. The uranium speciation in the stream waters has been studied in a modelling exercise *[Duffield et al., 1988]*. It was found that all uranium was present in the hexavalent form. The computer simulations predicted that the equilibrium pH should be at 8 whereas the field data showed pH-values just below 7. It was concluded that either the experimental data were incomplete or the simulations did not include all relevant pH-buffering components. The pH was found to have a significant effect on the uranium speciation as the predominant species at the model-predicted pH of 8 would be carbonate complexes while they at the experimentally determined pH 7 would be phosphate complexes. Further research to account for effects like sorption, colloid formation and complexation with organic ligands was recommended.

The same group *[Duffield et al., 1988]* also modelled the speciation of uranium around redox fronts found in deep-sea sediments sampled at the Madeira Abyssal Plain Natural Analogue sites. The upper 18 cm of the sediments have been found to be oxidising whereas reducing conditions prevail below this level. The chemical speciation modelling showed that a redox potential below -296 mV was required to precipitate amorphous uranium dioxide whereas crystalline uraninite was predicted to form below +27 mV. The modelling group concluded that an intermediate form between amorphous and crystalline would be consistent with the slightly reducing conditions observed in the sediments. The uranium in the aqueous phase is predominated by carbonate complexes. In the first modelling attempt significant concentrations of pentavalent uranium appeared. As this species is known to be stable only in acidic environments (e.g. *[Grenthe et al., 1992]*) and to disproportionate into quadrivalent and hexavalent uranium at higher pH, a second modelling attempt excluding the pentavalent uranium species was made. In this second attempt hexavalent uranium was found to predominate down to an E_h of -400 mV.

3.2.2 Conclusions

Thermodynamic equilibrium models have been applied to data from natural analogue studies both for model validation purposes and within the site interpretation process. One way to use the model in the interpretation of the site is to study the saturation situation with respect to different minerals and then use this in the tracking of the source of certain trace substances, to describe the transport paths that are active at the site and so on. Although such applications have no direct connection with the modelling performed in performance assessments, they contribute to the experience in applying thermodynamic equilibrium models and to develop the data bases necessary for such modelling. The general understanding of geochemical systems that such applications give rise to is important for the credibility of the performance assessment. The analyses of Alligator Rivers, Broubster and Needle's Eye mentioned above are typical examples of this use of models.

The analyses of data from Poços de Caldas, Oman, Maquarin and Cigar Lake are more oriented towards model validation. The procedure has been to supply the modelling groups with the concentrations of major species and the values of master variables in groundwater samples from the site and then to let the modelling groups predict trace element concentrations. Only the Poços de Caldas and Cigar Lake data have allowed a real comparison between model predictions and analytical data from the site. In the Maquarin study the analyses from the site have not yet been compiled and supplied to the modellers, and in the Oman case most of the groundwater samples had trace-element concentrations below the state-of-the-art detection limits. The modelling exercises quoted indicate that the different geochemical computer codes used have behaved similarly and that the differences in the modelling results can be deducted from differences in data bases and the chemical reactions accounted for.

There was reasonable agreement between calculated and measured trace element concentrations from all sites. Most of the deviations were such that the calculated concentrations were above the measured. The predictions were thus conservative from a solubility point of view. There could be several reasons for the conservative predictions such as omission of solubility-limiting phases from the data base. The real solubility limiting phase could be poorly thermodynamically characterised or simply unidentified. Solid solutions, mixed minerals, coprecipitation products etc could play important roles.

The differences were greater between the aqueous speciations calculated by different groups than between the calculated total trace-element concentrations. In particular for uranium indicating that there still exist uncertainties in the speciation data bases. There has been no opportunity to compare calculated aqueous speciations with field data on speciation. Techniques for separating different species were applied at Poços de Caldas with limited success. As long as reliable analytical techniques for analysing the speciation are lacking, the total elemental concentrations of the trace elements will be the only object function available for model validation.

Several areas that are poorly described by the models have been identified. These include the formation of colloids, coprecipitation and complexation with organics.

3.3 Functional dependencies of groundwater redox conditions

3.3.1 Background and hypothesis

The redox conditions in the groundwater is a very important parameter which strongly influences the solubility and the tendency for sorption of several important radionuclides. The presence of ferrous iron in the rock minerals and in the groundwater has been used as an indicator that deep groundwaters in crystalline rock are generally reducing. Consequently the solubilities of e.g. uranium, neptunium and technetium are considered low (teravalent state) and their tendency to sorb onto rock surfaces are regarded to be high.

The importance of the redox conditions has caused much work to be invested into the determination of the redox potential. Many workers have compared measured redox potentials, E_h-values, with those calculated on the basis of different redox couples. They often found that the measured potentials could not be matched with any of the calculated values. They therefore concluded that the natural system was not in equilibrium and that the potential thus could not be measured. In later work it has been shown that the method used to measure the redox potential is crucial *[Wikberg, 1987; Wikberg, 1991; Grenthe et al., 1991]* since trace amounts of oxygen can ruin the measurements. It has been concluded that it is easier to obtain reproducible values in downhole measurements than in measurements at the surface *[Wikberg, 1987]*. If measurements at the surface are made, it might be necessary to equilibrate the electrodes for a substantial period of time (approx. 10 days) after they have been in contact with air.

In a recent paper *[Grenthe et al., 1991]* all E_h measurements carried out in the mobile field laboratory used in SKB's field investigation programme have been modelled. It has been concluded from this exercise that the redox potential can be measured and that it is controlled by the equilibrium between ferrous iron in solution in the water and crystalline forms of ferric iron.

There are indications that this model is valid in groundwaters with strongly varying chemical characteristics. This hypothesis is tested below by applying the model to groundwater analyses from a number of different natural analogue studies.

3.3.2 Analysis

The model proposed by *[Grenthe et al., 1991]* is based on the observation that the redox conditions in deep Swedish groundwaters are buffered by the equilibrium between ferrous iron, Fe^{2+}, and precipitated ferric iron hydroxide, $Fe(OH)_3(s)$. Both laboratory and field experiments have shown that stable and reproducible measurements can be obtained in deep groundwaters, with a precision of ± 25 mV. The proposed model is valid for systems with a Fe(II) content of >0.05 ppm. In groundwaters with a high content of carbonate the complexation of Fe(II) with carbonate should be considered in the analysis since this may reduce the free concentration of Fe^{2+} in the groundwater. The presence of sulphide in concentrations up to about 10 ppm is expected to have insignificant influence on E_h measurements with platinum or glassy carbon electrodes, whereas, gold electrodes should not be used in the presence of sulphide. It has also been shown that very small amounts of dissolved oxygen in the groundwater, e.g. as contaminants from drilling, will significantly disturb the E_h measurements.

The analysis presented here is based on various data reported from the natural analogue sites at:

- Osamu Utsumi mine and Morro do Ferro mine at Poços de Caldas, Brazil,
- Nizwa Jill, Karku, Jebe Awq, Nidab and Bahla, Oman,
- Alligator River, Australia,
- Palmottu, Finland, and
- Cigar Lake, Canada.

In the study reported data from site investigation studies have also been included such as:

- Finnsjön, Fjällveden, Klipperås, Forsmark and Äspö, Sweden,
- Böttstein, Weiach, Riniken, Schafisheim, Kaisten and Leuggern, Switzerland, and,
- Olkiluoto, Finland.

An addition to data from these sites, data from Broubster and South Terras, Cornwall, have been reviewed. The model by *[Grenthe et al., 1991]*, see below, has been found to match the data from these sites poorly. The model yields E_h-values that exceed the measured values with several hundred mV. An analysis of these findings shown that the water samples probably have been exposed to oxygen, and that the redox couple Fe(II)/Fe(III) therefore does not govern the redox conditions in the way assumed in the model.

The model by *[Grenthe et al., 1991]* assumes in its simplest form that no complexation of Fe^{2+} takes place. Then the following formula is valid for the redox equilibria $Fe^{2+}/Fe(OH)_3(s)$:

$$E_h=E_0^*-\ln(10)\bullet R\bullet T/F\bullet(\log[Fe^{2+}]+3pH)$$

where $E_0^*=0.707$ V, which has been determined by *[Grenthe et al., 1991]* using field data from the Swedish site investigations *[Wikberg, 1991]*.

[Grenthe et al., 1991] also propose a simple method to compensate for complexation of Fe^{2+} with CO_3^{2-} according to the expression:

$$[Fe^{2+}]=[Fe(II)]_{total}/(1+\beta\bullet[CO_3^{2-}])$$

where $\beta=5.56$ *[Bruno et al., 1992]*.

In the present study this expression has been slightly modified so as to use $[HCO_3^-]$ which is more frequently reported than $[CO_3^{2-}]$. The expression then reads:

$$[Fe^{2+}]=[Fe(II)]_{total}/(1+[HCO_3^-]\bullet 10^{(pH+\log K)})$$

where $\log K=-4.77$ for the reaction $Fe^{2+} + HCO_3^- \rightleftarrows FeCO_3^0 + H^+$

As a variation and extension of the model by *[Grenthe et al., 1991]*, the redox potential has been calculated for different solid ferric minerals. The hypothesis has been tested, that different ferric minerals may determine the redox potential at different sites, depending on the age and crystallinity of the solid. Generally, well crystallised solids have lower solubility, resulting in lower redox potential than fresh or amorphous precipitates. Solid mineral phases ranging from freshly precipitated ferric hydroxide, $Fe(OH)_3$(ppd), to well crystallised goethite, FeOOH(cr), have been used in the calculations.

Poços de Caldas, Brazil

The data reported for Osamu Utsumi mine and Morro do Ferro mine in Poços de Caldas (PdC), Brazil, have been tested with the model by *[Grenthe et al., 1991]*. A comparison between the calculated results, with and without compensation for carbonate complexation, and the measured redox potentials shows that in all readings the measured redox potentials are higher than the calculated values for the $Fe^{2+}/Fe(OH)_3(s)$ redox couple. The compensation for carbonate complexation gives only slightly improved values. The equilibrium Fe^{2+}/Fe^{3+} has also been tested by directly adopting the analysed data without consideration to any speciation effects. The measured potentials are in this case lower than the calculated except in a few readings for shallow ground waters. The same data have, however, been analysed in a more comprehensive way using the thermodynamical equilibrium program PHREEQE within the Poços de Caldas natural analogue project *[Nordstrom et al., 1990]*. The calculated redox potential for Fe^{2+}/Fe^{3+} determined by speciation of the Fe(II) and Fe(III) data is in good agreement with the measured redox potentials. *[Nordstrom et al., 1990]* comment that $Fe(OH)_3(s)$ is supersaturated in many of the calculated waters with $pH>5.5$-6. This is possibly explained by the occurrence of ferrihydrite particles in the Fe(III) analyses.

In Figure 3.1 calculated results using the extended model described in previous section, are compared with measured redox potentials. It can be concluded that the measured data are in quite good resemblance with the calculated values for $Fe(OH)_3$(ppd). Considering the present active stage of continuous oxidative weathering of the rock at Poços de Caldas, the presence of $Fe(OH)_3$(ppd) is expected and may well be the redox buffering system at this site.

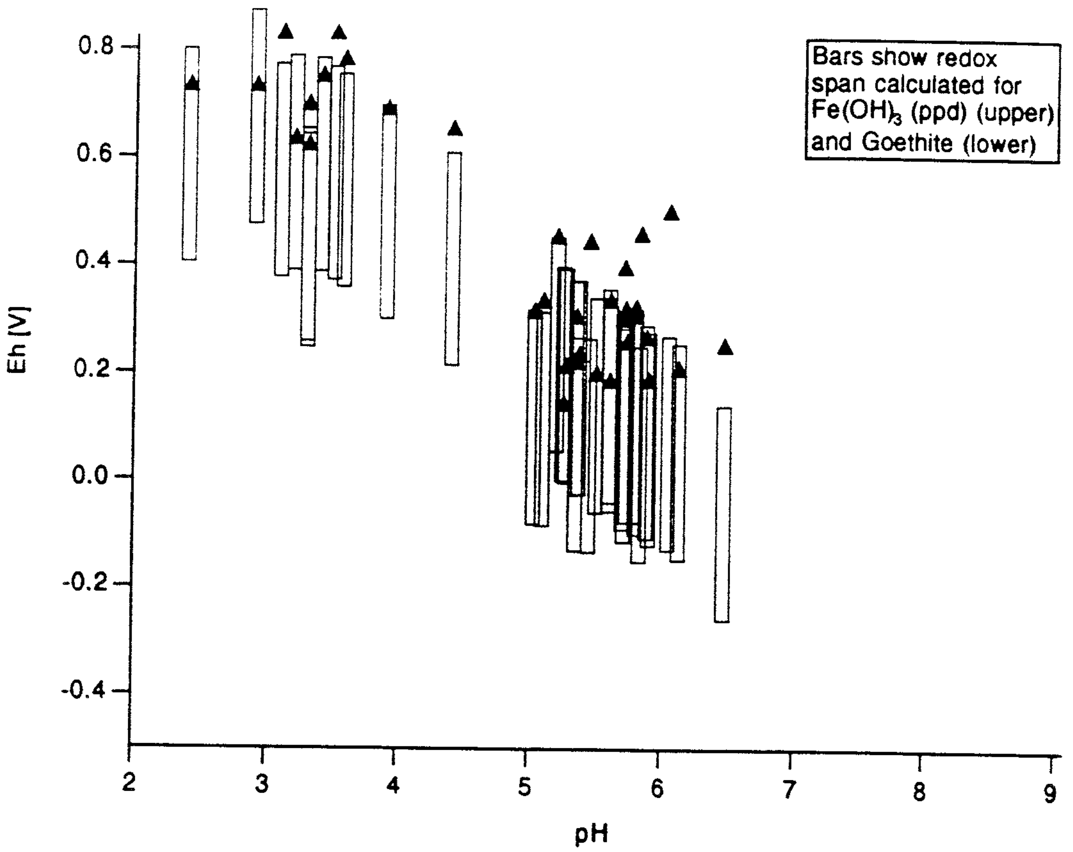

Figure 3.1 Comparison between redox potentials measured at Poços de Caldas and the range of redox potentials calculated for different ferric minerals.

Conclusions from the analysis using groundwater data from Poços de Caldas are:

- by applying the model by *[Grenthe et al., 1991]* with the assumption that Fe(II) is predominantly in the form of Fe^{2+} and that Fe^{3+} is given by equilibrium with $Fe(OH)_3(s)$, the calculated redox potentials are far below the measured values,

- compensation for complexation with carbonate only slightly improves the calculated results due to low carbonate content in the groundwater at this site,

- extending the model by *[Grenthe et al., 1991]* to include a range of ferric iron minerals, a good resemblance with measured data has been calculated for freshly precipitated $Fe(OH)_3$(ppd). This is in accordance with expectations from geologic observations of ongoing oxidative weathering of the rock,

- the use of speciation models to determine the free concentration of Fe^{2+} and Fe^{3+} appears to be a valuable approach for the chemical conditions at Poços de Caldas, c.f. *[Nordstrom et al., 1990]*, but requires that measures are taken in the preparation of groundwater samples so that solid ferrihydrite particles are not introduced in the $Fe(III)_{total}$ or Fe_{total} analyses and

- sampling procedures must ensure that contamination by oxygen from the atmosphere does not disturb the redox potential measurements.

Oman

The Oman waters are low in iron, <0.01 ppm, probably due to the primary formation of $Fe(OH)_2$ which then possibly is transformed to haematite magnetite *[Bath et al., 1987]*. The model by *[Grenthe et al., 1991]* has been applied assuming an Fe(II) content of 0.01 ppm, which results in predicted redox potentials of 500 mV or more below the measured values. For this low (and uncertain) iron content the model is not expected to be valid.

As a second attempt it was instead assumed the Fe^{2+} may be controlled by dissolution of $Fe(OH)_2$(ppd) in the alkaline environment. The solubility was calculated from:

$$\log Fe^{2+} = 12.85-2\bullet pH$$

The calculated redox potentials were considerably closer to the measured values. An even closer fit was obtained assuming equilibrium with FeO(s), $\log Fe^{2+} = 11.36-2\bullet pH$.

The Oman waters are, however, expected to contain sulphide, possibly due to the action of sulphate reducing bacteria. It is, therefore, possible that the redox buffering is obtained by bacteria mediated SO_4^{2-}/H_2S reaction in the Oman waters. Contamination by atmospheric oxygen can not be excluded. In conclusion, the data from Oman, in particular the absence of quantitative analyses of Fe(II), do not allow for application of the model by *[Grenthe et al., 1991]*. The pH of the Oman waters are also outside the range of application of the model. The modification of the model, assuming equilibria with $Fe(OH)_2$(ppd) or FeO(s) improved significantly the fit with measured data, although this may be coincidental.

Alligator River

The model by *[Grenthe et al., 1991]* has been applied on the Alligator River Analogue Project (ARAP) data, assuming that all iron is present as Fe^{2+} and that Fe^{3+} is determined by equilibrium with $Fe(OH)_3$(s). Poor correlation with measured redox potentials was found. In almost all analysed samples the calculated and measured redox potentials differ by 200-500 mV, in some cases up to about 700 mV. In all cases the calculated redox potentials are lower than the measured readings. In some of the samples traces of dissolved oxygen is reported.

However, when using the extended model, as described in previous sections, a striking correlation between measured data and values calculated for $Fe(OH)_3$(ppd) has been found, see Figure 3.2. It can be noted that major deviations between measured and calculated data occur above approximately pH 7.5.

It can be concluded that the ARAP data are not sufficient for application of the model by *[Grenthe et al., 1991]*. Fe(II) determinations are not available and traces of oxygen have been reported in some samples. Speciation calculations may improve the correlation between measured and calculated redox potentials, but no such calculations have been made within this study. By assuming that the reported iron is present mainly as Fe^{2+}, the resemblance between measured redox potentials and calculated values assuming freshly precipitated ferric hydroxide is promising, although some data points above pH 7.5 show deviations.

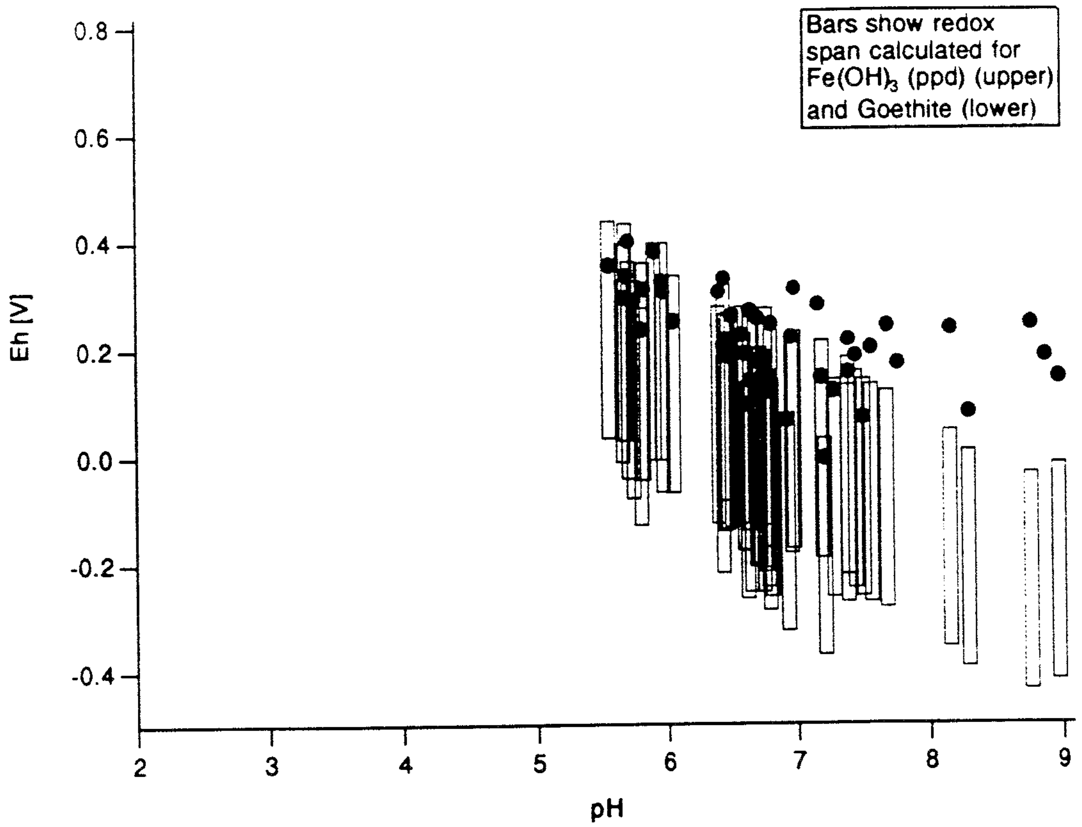

Figure 3.2 Comparison between of measured and calculated redox potentials for the Alligator Rivers natural analogue site.

Palmottu

Only two complete sets of data have been reported *[Suksi et al, 1992]* which allows for application of the model by *[Grenthe et al., 1991]*. The agreement between measured and calculated redox potentials is reasonable with differences of 210-230 mV. In one of the samples dissolved oxygen was found. It may be interesting to study the redox conditions using down-hole measurements by the method described by *[Wikberg, 1987]* and *[Grenthe et al., 1991]*.

Using the extended model described earlier, the two measured data points are well within the range of calculated values for the different solid ferric minerals. No firm conclusions should be drawn based on the two measurements.

Some thermodynamic modelling has been made for the Palmottu data within the Finnish study *[Suksi et al, 1992]*, where good correlation was found between the measured redox potentials and the $Fe^{2+}/Fe(OH)_3(s)$ equilibria. Once again, this points out the value of speciation modelling of the analysed data.

It has been pointed out *[Ahonen et al., 1992b]* that the redox potentials measured at Palmottu agree well with the equilibrium redox potential of the transition between tetravalent and hexavalent uranium. This could indicate that uranium plays a role in the redox system at this site. The authors, however, comment that the findings do not serve as a proof of Nernstian behaviour of soluble uranium even if equilibrium between the two valencies seems to be attained.

Cigar Lake

The model by *[Grenthe et al., 1991]* has been applied on the Cigar Lake data, but poor correlation with measured redox potentials was found. In many analysed samples the calculated and measured redox potentials differ by more than 200 mV, in some cases more. In all cases the calculated redox potentials are lower than the measured readings. In a number of samples traces of dissolved oxygen is reported.

However, when using the extended model, as described in previous sections, most measured data fall within the range of calculated values, see Figure 3.3. The data are scattered over the whole range of redox potentials calculated for different solid phases, i.e. from $Fe(OH)_3$(ppd) to crystalline goethite. This may indicate that different ferric iron minerals are active redox buffers at different locations in Cigar Lake.

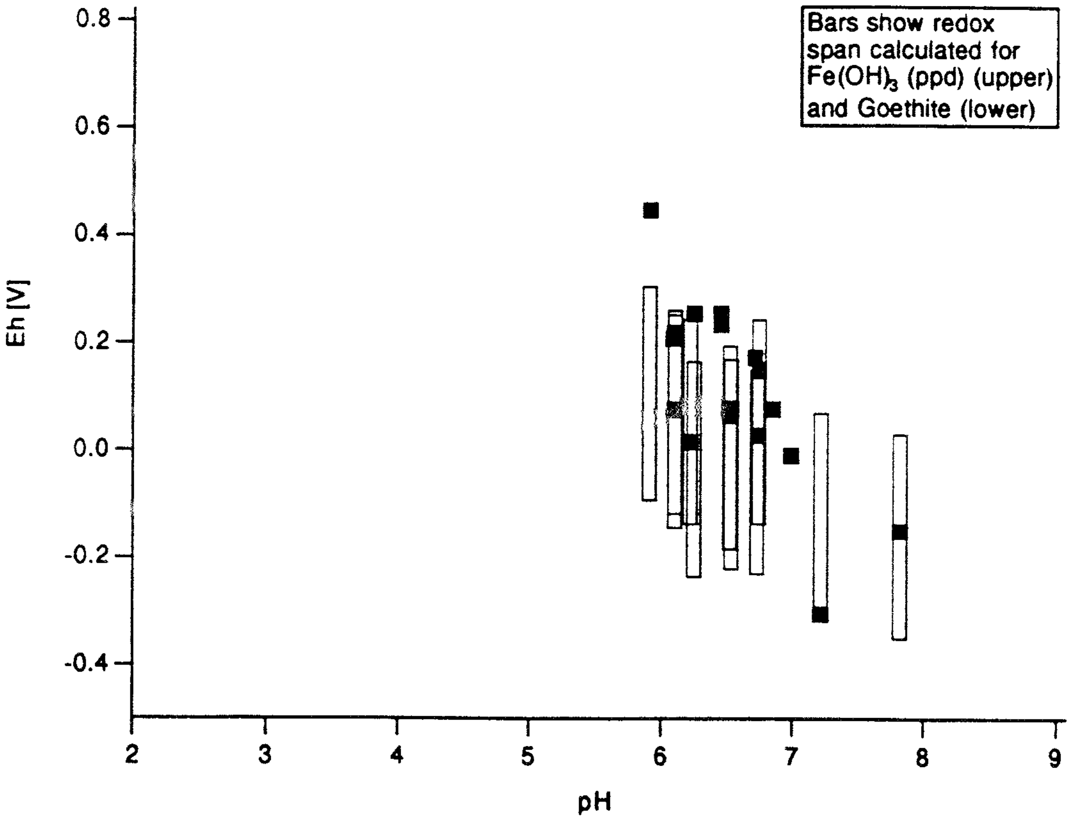

Figure 3.3 Comparison of measured and calculated redox potentials for groundwater samples from the Cigar lake natural analogue site.

SKB site investigations

A special down-hole measurement technique was developed within the SKB program to obtain reliable measurements with as little contact with the atmosphere as possible *[Wikberg, 1987]*.

Application of the model by *[Grenthe et al., 1991]* to these data shows an excellent agreement between measured and calculated redox potentials for the $Fe^{2+}/Fe(OH)_3(s)$ equilibria.

Using the extended model the calculated values clearly indicate the close resemblance between measured data and the redox conditions determined by old, well crystallised precipitates of ferric minerals, e.g. goethite. The results are presented in Figure 3.4.

The conclusions that can be drawn are:

- the *[Grenthe et al., 1991]* model is applicable to the deep Swedish groundwaters,
- correction for carbonate complexation further improves the agreement with measured data,
- using the extended model described in previous sections, all measured data points except one, are within the range of calculated values,
- careful experimental techniques greatly improve the value of field measurements, and
- redox conditions in deep Swedish groundwaters appear to be buffered by $Fe^{2+}/Fe(OH)_3(s)$ equilibria, possibly aged, well crystallised goethite.

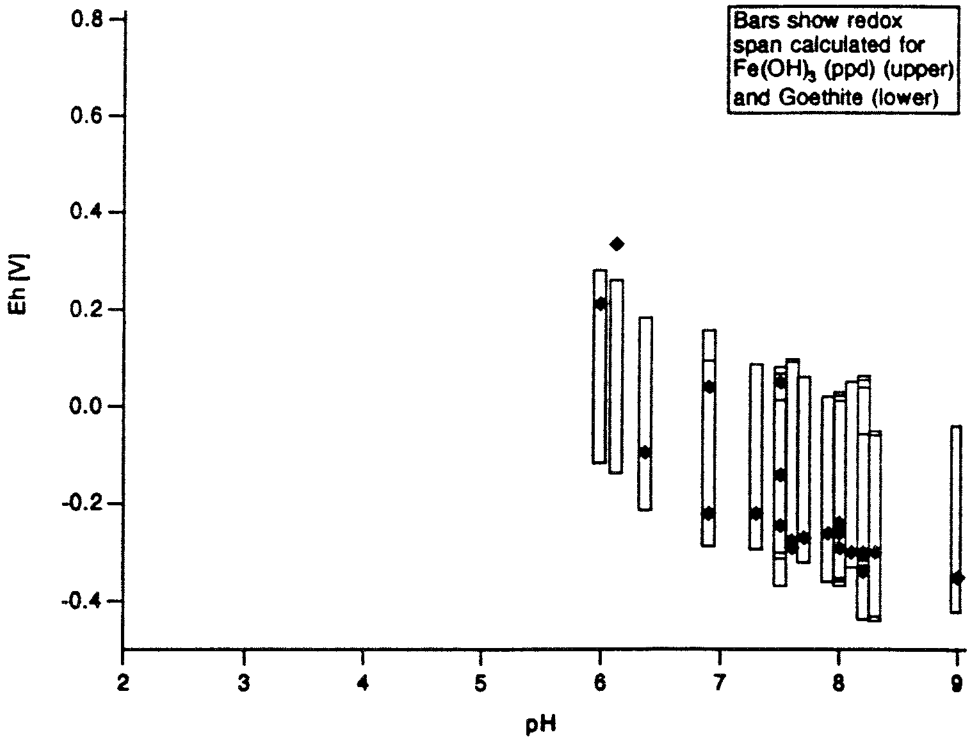

Figure 3.4 Comparison of redox potentials measured in deep Swedish groundwaters and values calculated for a range of ferric minerals.

Swiss site investigations

The agreement between measured and calculated redox potentials using the *[Grenthe et al., 1991]* model is generally low. A reasonable agreement has been found for some data points, but this may be coincidental. Major disturbance in the analysed data may be the reported traces of dissolved oxygen in some waters. In *[Pearson et al., 1989]* various redox couples were investigated, but no firm conclusions regarding redox buffering in the different systems seem to have been reached, although the arsenic couple and the uraninite system show some similarity with the measured redox potential using platinum electrode.

Using the extended models described in previous sections, the majority of the measured data falls within the range of calculated values assuming different solid ferric minerals. About 20 of the 32 data points closely resembles the values calculated for freshly precipitated ferric hydroxide, 6 values suggests redox conditions related to old, crystalline forms of ferric minerals, e.g. crystalline goethite, whereas, the remaining data points are in the middle of the calculated range of redox potentials. No measured data exceeds the calculated range of redox potentials by more than about 50 mV, and only one data point falls below the calculated range.

The conclusions are:

- the model by *[Grenthe et al., 1991]* is not applicable to the Swiss data,
- calculations using the extended model described in previous sections indicate that different ferric minerals may determine the redox conditions in the different samples. This conclusion is not firm, but all 32 samples have been found to correlate reasonably well with the calculated range of values,
- traces of oxygen in the samples may be due to contamination, resulting in too high values being measured, or,
- other redox couples, e.g. As(III)/As(V) or $UO_2(s)$/U(VI) may buffer the redox conditions.

Olkiluoto site investigations

Redox potentials calculated by the model *[Grenthe et al., 1991]*, usually differs by more than -200 mV from the measured redox potentials. In a few readings the agreement is quite good but this appears to be coincidental. The analysed waters in many cases contain dissolved oxygen, which may explain the difference between measured and calculated redox potentials.

Using the extended model described in previous sections, it has been found that 7 out of 9 data points fall within the range of calculated data. Two data points exceed the calculated range by about 100 mV. This indicates that the groundwater redox conditions may well be determined by the $Fe^{2+}/Fe(OH)_3(s)$ redox couple. Most data points are in the low to middle range of the calculated interval, indicating an old groundwater, possibly determined by crystallised forms of ferric minerals, e.g. goethite.

Thermodynamical modelling has been made for these water samples *[Pitkänen et al, 1992]*. The results show that Fe(II) is found mainly as sulphide complexes in the most reducing waters, some doubts regarding the reliability of the thermodynamic data for the complexation reactions are expressed by the authors. Attempts are also made to correlate the measured data with the

$CH_4(g)/HCO_3^-$ redox couple, but with limited success. It is commented that the low content of iron indicates that Fe(II)/Fe(III) is not the major redox buffering factor in these waters. Calculations assuming pyrite, which is frequently found in the rock, as a redox buffering solid give more satisfying correlation with measured data.

3.3.3 Conclusions

The analysis in the previous section shows, that strong indications exists that the redox potential in a variety of groundwaters is controlled by equilibrium between ferrous iron in solution and solid ferric iron minerals. Substantial amount of data to support this conclusion has been collected from ongoing studies of natural analogues. The study of natural analogues have in this sense provided a unique opportunity to test the applicability of different redox models on a variety of chemical conditions and in groundwater systems of different age.

The model by *[Grenthe et al., 1991]* appears to apply in the first hand to old groundwaters, like those found in Fennoscandia. An extended model has been suggested within this project which has been applied to a variety of groundwaters with different chemical compositions. The extended model has been found very useful when applied to the analysed data from the various natural analogue studies. It can be concluded that:

- the deep groundwaters in Sweden correlate very well with redox potentials calculated for aged and well crystallised ferric minerals, e.g. goethite, suggesting that the geological changes in the deep groundwater are very slow,

- the extended model has been found applicable to Finnish conditions, although other redox couples may also be active in some of the waters,

- the model has been tested on data for groundwater systems which appear to be at rest, e.g. Swedish and Finnish groundwaters, as well as on data for groundwaters where weathering reactions are currently active, e.g. Poços de Caldas and Alligator Rivers. The groundwaters at the different sites also have varying contents of carbonate and sulphide, and pH ranging from less than 3 to 9,

- the general applicability of the model is indicated by the close fit with almost all studied data from a variety of sites with different groundwater characteristics. It may be argued that individual data points do not fall within the calculated range of redox potentials, but considering the wide range of geochemical conditions represented by the different groundwaters, the overall pattern seems quite convincing.

The testing of the models on data from the different natural analogue sites and the repository site investigations have pointed out the possibility to determine the redox conditions of groundwater systems based on simple chemical analyses of pH, Fe(II) and carbonate. The simple chemical analyses, which can be made in the field, are sufficient for the analysis. Comparing the calculated redox potentials with field measurements and geological observations, a reliable picture of the redox conditions in the rock can be obtained. The simplicity of the chemical analyses is the major advantage of this method. The study had also pointed out the usefulness of geochemical speciation modelling as a tool for increasing the understanding of the redox conditions in groundwater systems.

It is important to recognise that the model results should be interpreted and compared with geological observations, e.g. the presence of different fracture filling minerals, their age and their crystallinity. It should furthermore be noted that the redox system is sensitive to trace amounts of oxygen in the samples. This is a likely reason for the poor agreement between the measured and calculated redox potentials from South Terras, Cornwall and Broubster.

To summarise, the data available from natural analogue studies offer a unique possibility to study and test the general applicability of different conceptual models and the validity of used geochemical data.

4. Radionuclide chemistry and transport in the near field

4.1 Background

In an underground repository the waste will be surrounded by engineered barriers. The main purpose of these barriers is to prevent contact between the waste and flowing groundwater and to constitute a transport resistance to dissolved radionuclides eventually leached from the waste. To predict the long-term performance of the barriers and the transport through the barriers various models are used. These models are based on extrapolations in time of initial barrier properties considering potential degradation mechanisms due to future changes in geological, hydrological and hydrochemical conditions at the site. The study of natural analogues gives an opportunity to test the validity of these models and their underlying assumptions in a long-term perspective.

The models used to describe the fuel dissolution in different safety analyses performed in the past (e.g. KBS-3 *[SKB, 1983]*, SKB 91 *[SKB, 1992a]* and TVO-92) assume that oxidising species are formed by α-radiolysis of the groundwater as it comes into contact with the uranium pellets in the spent fuel subsequent to canister penetration. The oxidising species, e.g. hydrogen peroxide, cause an oxidation of the UO_2 to hexavalent uranium that is more readily soluble in the groundwater than is the UO_2. The oxidised uranium and the oxidising species formed by the radiolysis are transported away from the spent fuel oxidising the content of ferrous iron in the surrounding rock. This creates an outward moving front between a zone with an oxidising environment around the spent fuel and the surrounding rock containing unaffected ferrous iron.

The release rate for oxidised (hexavalent) uranium from the canister is likely to be limited by the solubility of schoepite, $UO_3 \bullet 2H_2O(s)$. Other solid phases of hexavalent uranium such as schoepite monohydrate, rutherfordine, silicates and phosphates could in principle also form.

Radionuclides embedded in the spent fuel matrix can also be exposed to water even if the matrix is not completely dissolved. Oxidation of UO_2 to higher uranium oxides above U_3O_7 changes the crystal lattice structure. Either dissolution of the UO_2-matrix or change of the crystal lattice due to oxidation could cause liberation of nuclides contained in the original UO_2 matrix.

Due to interaction between radioelements and corrosion products from steel containers, mainly iron oxyhydroxides, a significant retardation of radioelements may occur. The primary mechanism is expected to be the well known scavenging effect of hydrous ferric hydroxide, $Fe(OH)_3$, which carries down various aqueous substances despite their expected higher solubility. The general mechanism of such coprecipitation can be described as a sequence, where ferric hydroxide is formed from a solution of ferrous iron (Fe(II)) and precipitates as a flocculent solid, onto which various solutes are adsorbed. The adsorbed substances may later form solid solutions with the carrier substance (e.g. $Fe(OH)_3$) whereby a permanent immobilisation can be expected. The adsorbed substances may also be physically embedded as a result of further precipitation of carrier substance (e.g. $Fe(OH)_3$). It is, however, important to demonstrate that the embedded substances are not expelled from the solid material if this undergoes some kind of transformation, recrystallisation.

The study of natural analogues offer an opportunity to identify the processes that are important and to validate parts of the models used to describe the processes. In this chapter, a review of evidence from natural analogues regarding the extent and effects of radiolysis, the formation and propagation of redox fronts, the behaviour of radionuclides at the redox front and their possible interaction with corrosion products as well as the diffusion of radionuclides through clay materials is presented. It has not been the ambition to make a complete review. Neither does the review cover all phenomena of importance to the near-field performance.

4.2 Radiolytic formation of redox agents

In the studies of the Oklo and Cigar Lake natural analogues analysis of the effects of the radiolysis phenomenon forms part of the main study objectives. The situation with regard to the radiation environment is significantly different at the two sites. At Oklo β-radiation predominated over α-radiation during the period when the natural reactors were operating. At Cigar Lake the relative contribution from α-radiation to the total radiation dose is significantly higher. It has not been conclusively analysed whether this is a reason for the apparently different effect of the radiolysis at the two sites.

In the reactor zones at Oklo, iron appears to have been reduced, possibly by hydrogen formed by radiolysis during the operational period of the reactor, whereas a portion of the uranium and some fission products with multiple redox states (e.g. Mo, Tc and Ru) seem to have been mobilised by oxidation and migrated away from the reactor zone. Some of the mobilised elements have subsequently been precipitated within a few metres from the reactor zones as the redox conditions change.

The reduction to ferrous iron observed at Oklo appears to be contradictory to the results of the near-field model. It is speculated in *[Curtis and Gancartz, 1983]* that the iron in the minerals at Oklo has been less accessible to the oxidising radiolysis products than to the more mobile hydrogen. Thus the hydrogen has, according to the hypothesised scenario, diffused into the solid material and caused the reduction of the iron. The authors suggest that the oxidation and mobilisation of fission products is caused by oxidising radiolysis products formed on the surfaces of the uraninite grains, and that the fission products migrated to the grain surfaces by solid-state diffusion, and that they were injected into the groundwater by fission recoil. Since the mineral host and the source of radioactive emissions were one and the same, the fission products at the grain surfaces were literally immersed in radiolysis products.

For Oklo the radiation dose to the groundwater and the yield of radiolysis products have been estimated *[Curtis and Gancartz, 1983]*. It was concluded in the KBS-3 study that the radiolysis in the investigated reactor zone at Oklo was 100-500 times lower than was estimated by theoretical calculations for a comparable quantity of fuel and a comparable burnup *[Christensen and Bjergbakke, 1982; SKB, 1983]*. The radiolysis yield in the reactor zone at Oklo was estimated from the observed amount of iron reduction assuming iron(III) had been reduced by radiolytically generated hydrogen. An observed loss of 10% of the uranium was attributed to radiolytic oxidation. Later mineralogical investigations have indicated the occurrence of a redox front at the boundary of an Oklo reactor (zone 10) *[Menet et al., 1992]*.

There has been no nuclear criticality in the Cigar Lake uranium deposit. The hydrothermal period was relatively short compared to the duration of its existence. Therefore, compared to Oklo, The Cigar Lake uranium deposit offers the possibility to study the effect of low level radiation at very long time periods and at ambient temperatures. Assuming radiolysis of water at the ore/clay contact, oxidants and hydrogen will be generated. Hydrogen is not very reactive at ambient conditions and is therefore expected to escape from the ore zone by diffusion through water in connected porosities in the ore and clay. Oxidants, generated by radiolysis, are for example oxygen and hydrogen peroxide. They are expected to react in the geochemical environment in and around the ore. The chemical conditions are in many respects similar to those in a spent fuel repository. Since hydrogen is expected to behave inert in a repository as well as in the Cigar Lake uranium deposit, the net chemical effect will be oxidation. Possible reductants have been identified at Cigar Lake in the groundwater, in the ore, in the clay and in the contact rock, see Figure 4.1 *[Karlsson et al., 1992]*:

- In the groundwater: Fe^{2+}, HS^-, DOC
- In the minerals: Fe(II) (e. g. siderite), sulphide (e. g. pyrite, galena), SOC (Solid Organic Content), U(IV) (uraninite)

At Cigar Lake a reddish aureole of ferric iron has formed around the uranium ore, see Figure 4.2. The ferric iron has been precipitated in the clay near the ore/clay contact as amorphous ferrihydrates and hematite *[Percival and Kodama, 1989]*. The uranium ore shows minor signs of surface alteration to mixed oxides of stoichiometries in the range of U_4O_9 to U_3O_7 *[Sunder et al., 1988]*. Dissolved oxygen and hydrogen have also been analysed in groundwaters sampled from the ore/clay zone. The signs of oxidation reactions and other products can, in principle be generated by radiolysis.

The observed oxidation at Cigar Lake is consistent with the postulated phenomena included in the near-field model described above. General radiolysis model calculations *[Christensen, 1990]* confirm that the radiolysis of water oxidise Fe(II) to Fe(III), which may then precipitate due to low solubility. The data produced in the Cigar Lake project should lend themselves to investigate whether the amount of ferric iron in the clay is consistent with the calculated radiation dose to groundwater and reasonable yields for the formation of radiolysis products. A comparison between a calculated production rate of oxidants due to radiolysis with the oxidant production rate required to oxidise the 1 m thick zone of the clay showed that the required oxidant production was only about 0.3 millionth of the calculated radiolytic oxidation rate. Therefore, if the observed oxidation of ferrous iron in the near-field at the Cigar Lake ore body is a result of radiolysis, then the total amount of ferric oxides generated is still minor compared to the predictions of the total net oxidation using models also employed to assess the amount of oxidation caused by spent fuel exposed to groundwater.

It is important to note the relatively small amounts of uranium that have become oxidised to higher valencies than uraninite compared to the large amounts of ferric iron in the aureole of reddish clay. However, laboratory experiments indicate that no radiolytic oxidation of uranium occurs at the uranium dioxide surface beyond a certain corrosion potential *[Shoesmith and Sunder, 1991]*. This may explain the lack of significant quantities of higher valency uranium oxides at the uraninite surfaces. As a consequence of the Cigar Lake observations the radiolytic model currently used for calculation of uranium oxidation by alpha radiolysis was modified by *[Christensen et al., 1992]*. It was shown that oxidation of UO_2 had been overestimated by an order of magnitude in the earlier calculations.

Oxidation of uranium ore (UO_2) to higher mixed oxides is of interest for understanding and modelling of the spent fuel leaching process. If oxidation continues above U_3O_7 to U_3O_8 it will alter the crystal lattice structure. Spent fuel consists of uranium dioxide with radionuclides contained in the crystal matrix. If the matrix is changed by oxidation these radionuclides may become exposed and available for dissolution. However, the evidence from Cigar Lake shows that only minor quantities of higher mixed oxides are present at the surfaces. Furthermore, the oxidation does not proceed above U_3O_7 which implies that the lattice structure remains unchanged.

An alternative reaction path leading to the exposure of radionuclides in spent fuel is the complete oxidation of uranium to U(VI) and subsequent dissolution as uranyl carbonate ions. However, there is no indication of extensive loss of uranium by oxidation to uranyl ions in the Cigar Lake deposit. Oxidation of U(IV) and Fe(II) are not the only oxidant-consuming reactions that can occur in the ore zone. In addition to oxygen consuming Fe^{2+}, the groundwater contain HS^- and DOC. In principle hydrogen and methane can also react with oxygen at ambient temperatures if the right microbes are present and active. The surrounding rock contains mineral reductants such as siderite (with Fe(II)) and various sulphide phases.

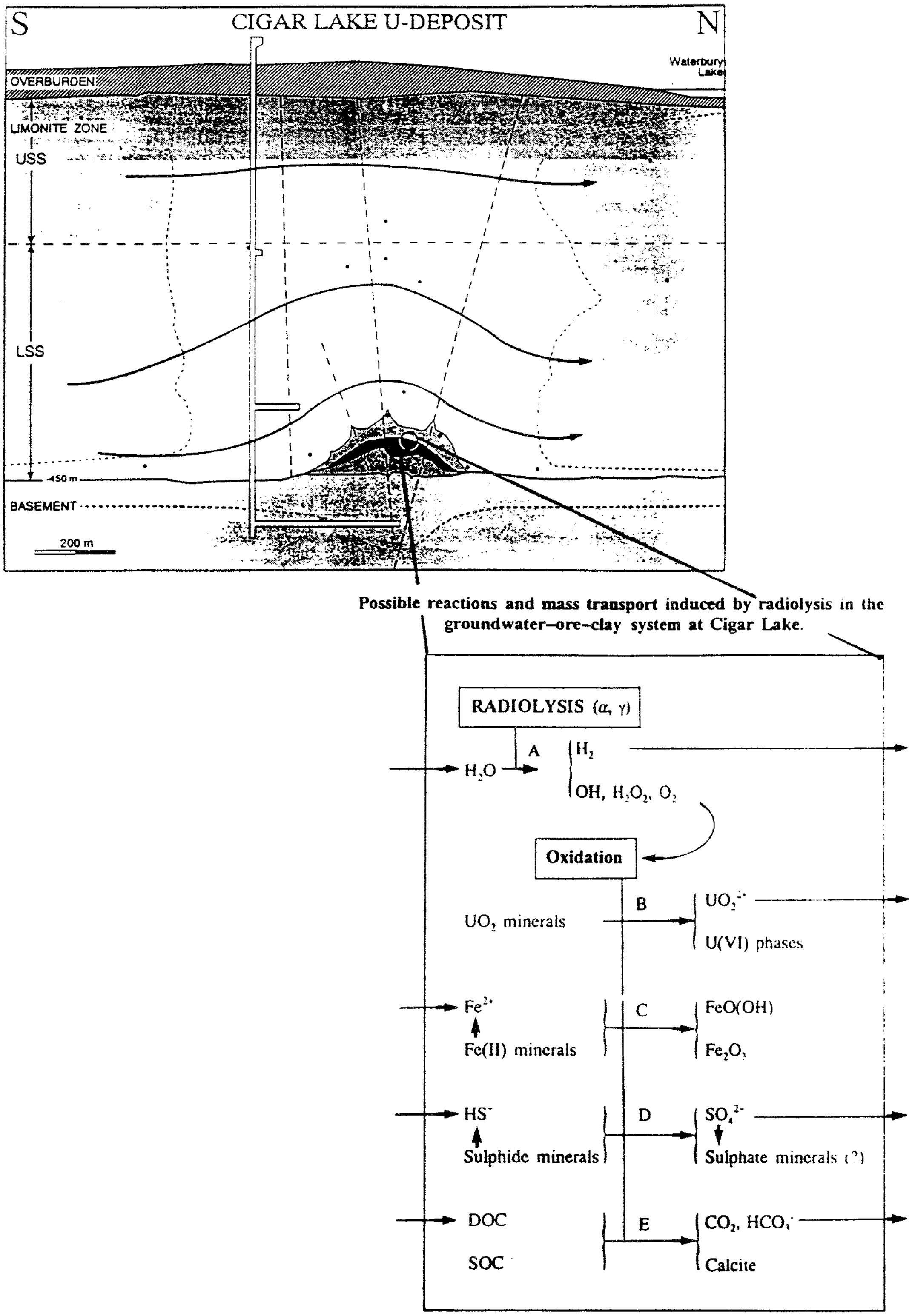

Figure 4.1 Diagrammatic vertical profile through the Cigar Lake uranium deposit showing the major rock units, the clay (c) and the ore (black) zones, the vertical shaft and main groundwater flow directions. The clay/ore contact, where radiolytic reactions might be expected is ringed (modified after *[Vilks et al., 1991]*). Schematically illustrated is an analysis of possible oxidation reactions caused by radiolysis; the production of hydrogen and oxygen (reaction A), and some possible oxidation reactions accounted by these species (reactions (B-E).

Figure 4.2 Drillcore through the clay halo surrounding the uranium ore at Cigar Lake. The clay close to the ore has been coloured by haematite (from *[SKB, 1992b]*).

The observations at Oklo and Cigar Lake support the following conclusions with regard to performance assessment of spent nuclear fuel disposal:

- Radiolysis of groundwater produces hydrogen and oxidising species. The yields are in general less than calculated by models (radiolysis kinetics).
- The net effect of radiolysis at ambient temperatures is oxidation because hydrogen does not react. This can create an oxidised near-field at the radiation source.
- Local radiolytical conditions at the surface of spent fuel can oxidise elements with multiple redox states (e. g. U, Mo, Tc and Ru).
- The assumption, that all oxidants produced by radiolysis are consumed by oxidation of UO_2 to higher uranium oxides with different crystal lattices, is overly conservative at least in the very long time perspective, when the dose rates are comparable to those of natural uranium.
- The reaction paths for the radiolytical produced oxidants and the near field reductants (e. g. UO_2, Fe^{2+}, HS^-, DOC, SOC, Fe(II) and sulphide minerals) are difficult to foresee. The kinetics of the possible redox reactions vary and the radiolysis is local. For example, alpha radiolysis is restricted to a thin layer on the radiation source. The redox reaction can occur at the source or the reactants can diffuse out in the near-field and react with the components there.

The results imply that radiolytic oxidation in the near-field of exposed spent nuclear fuel in an underground repository cannot be ruled out. However, the net changes have been considerably overestimated by the models which are used to describe spent fuel radiolysis and its consequences. The observation of oxidation in the ore body of Cigar Lake indicates that reactions with U(IV) in spent fuel will not necessarily consume all the oxidants generated.

4.3 Propagation of the redox front and radionuclide chemistry at the front

In the Osamu Utsumi mine the behaviour of different elements at the redox front have been extensively studied, both radioelements of the natural decay series and stable elements. At Morro do Ferro, the geochemistry of thorium, uranium and light rare-earth elements have been investigated.

In borehole F1 in Osamu Utsumi mine the redox front is found at several depths, with zones of oxidising conditions penetrating into the rock near major fractures. An upper oxidised zone is found from the surface down to 33.4 metres, followed by an upper reduced zone from 33.4- 42 metres, then a lower oxidised zone between 42 and 66.2 metres and finally a lower reduced zone from 66.2 - 75 metres, below which the rock is expected to represent background levels.

A sharp redox front is observed were Fe(II) (mainly pyrite) buffers the redox conditions. The oxidation of pyritic Fe(II) to Fe(III) is visible as a sharp colour change in the rock. The extremely sharp front indicates an almost complete reduction of oxidant within millimetres from the redox front. Soluble species expected to be less readily reduced, possibly due to kinetics (e.g. SO_4^{2-} and UO_2^{2+}), have been found to be reduced within a few centimetres from the redox front, see Figure 4.3.

A sharp increase in the uranium concentration is observed immediately on the reducing side of the redox fronts, indicating that uranium and iron redox reactions occur at almost identical locations in the rock. Oxidation of uranium at the redox front results in increased solubility of uranium, creating a concentration gradient which leads to diffusion of hexavalent uranium into the reducing rock where it reprecipitates, eventually forming nodules. However, uranium may also diffuse into the oxidising zone where it may be adsorbed by, or coprecipitated with, iron and manganese oxides. In fact uranium is found in increased concentrations also in the oxidising rock compared with the background levels in the deep reducing rock. Uranium in the hexavalent state would be expected to remain dissolved in the groundwater system, but is obviously removed from the solution. This has been interpreted as scavenging by precipitation of iron or manganese oxides *[MacKenzie et al., 1990]*.

The rate of movement of the fronts have been estimated to about 2-20 metres in $1 \bullet 10^6$ years. Dissolution of the uranium nodules have been estimated to require 10^4-10^5 years, whereas, the formation of the nodules would require at least 10^5 years.

Thorium has been found to be deposited in the first hand on the reducing side of the redox front but the effect of enrichment is much less pronounced than for uranium. Thorium is expected to be insensitive to redox conditions and to be practically insoluble.

Investigations of a large number of stable elements showed that non-redox sensitive rare earth elements (REE) in the trivalent and tetravalent states behave systematically and are concentrated at the reducing side of the redox fronts. Eu which is redox sensitive, behaves generally in the same way as the rest of the REE. Ce on the other hand appears to be subject to active redox reactions, Ce(IV)/Ce(III), and is enriched at the oxidising side of the redox front.

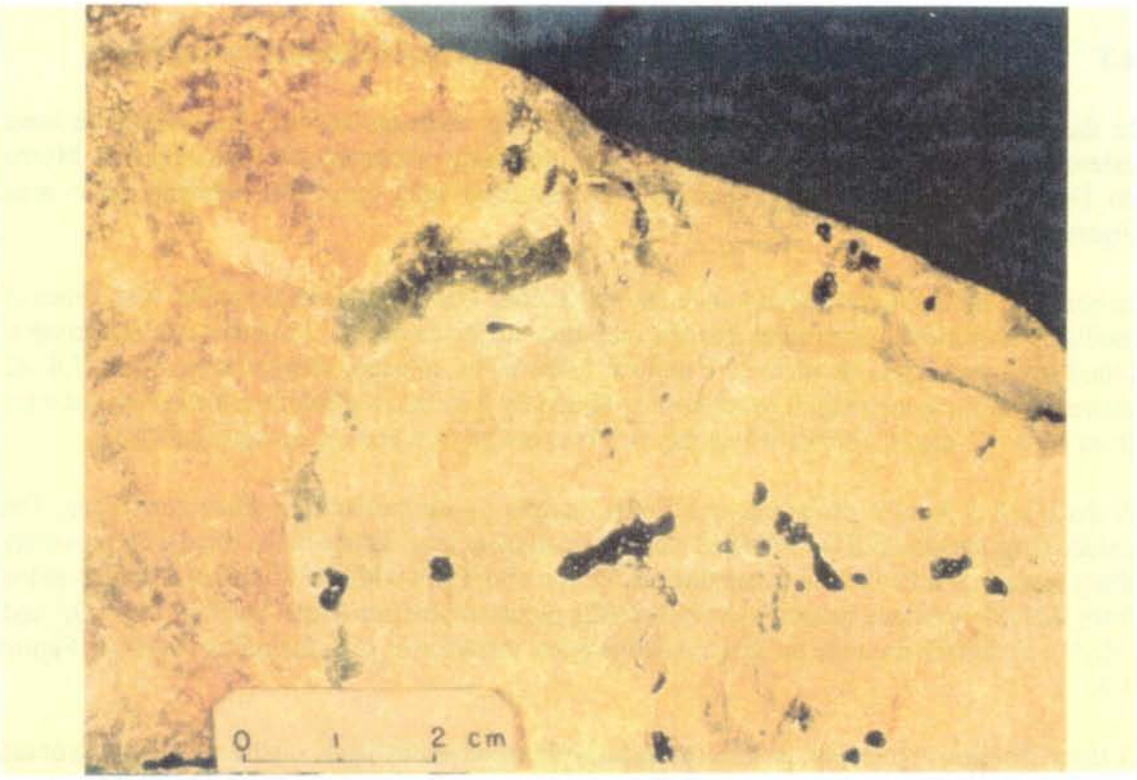

Figure 4.3 A piece of rock showing the colour change from the oxidising (left) to reducing side of the redox front at the Osamu Utsumi mine. The dark spots in the reducing zone represent pitchblende nodules that have been precipitated downstream of the redox front(from *[Chapman et al., 1991]*).

Some interesting notations have also been made been made by comparing the analysed data for all considered elements with the background levels in the reducing rock below 75 metres. It has been noted that iron is depleted in the upper reducing zone below the surface, which is to be expected from the higher solubility of ferrous iron. It is concluded that a number of systematic trends can be seen and that these are in accordance with the expectations for the position of the elements in the periodic table. Consequently, the most soluble elements (Mg, Ca, Sr) have been washed out by the groundwater from the upper 75 metres of the rock. The same behaviour is observed for the redox sensitive elements As and Mn, but also the trivalent elements La, Pr, and Nd, and the tetra-valent element Hf. Li and Ce are enriched in the upper reducing zone but depleted in the other zones. Y, Sm, Tb, Dy, Ho and Er are enriched in the upper reducing zone. The rare-earth elements Eu, Gd, Tm, Yb and Lu, the noble elements Os, Ir, Pt and Au, as well as Sc, Cu, Pb and B are enriched in the upper reduced zone and the lower oxidized zone but are depleted in the upper oxidised and lower reduced zones. The remaining elements are all enriched throughout the upper 75 metres of the rock. Figure 4.4 shows examples of concentration profiles across the redox front.

From other redox fronts studied within the same area it has been observed that:

- uranium has in one case (redox front 71ZE23) been found in significantly higher concentrations in the reduced zone than in the oxidised zone. In this case the low uranium concentrations suggest that uranium has been depleted in the oxidised zone rather than enriched in the reduced zone,
- a rather complex situation for uranium near the redox front has been found (redox front II), possibly indicating the importance of mineralogical variations in the rock,
- strong evidence is found (redox front NM) for dissolution of deposited uranium as the redox front moves into the reduced rock. Observations suggest that uranium is not necessarily precipitated at the redox front, but may diffuse a few centimetres further into the reduced rock before being precipitated.

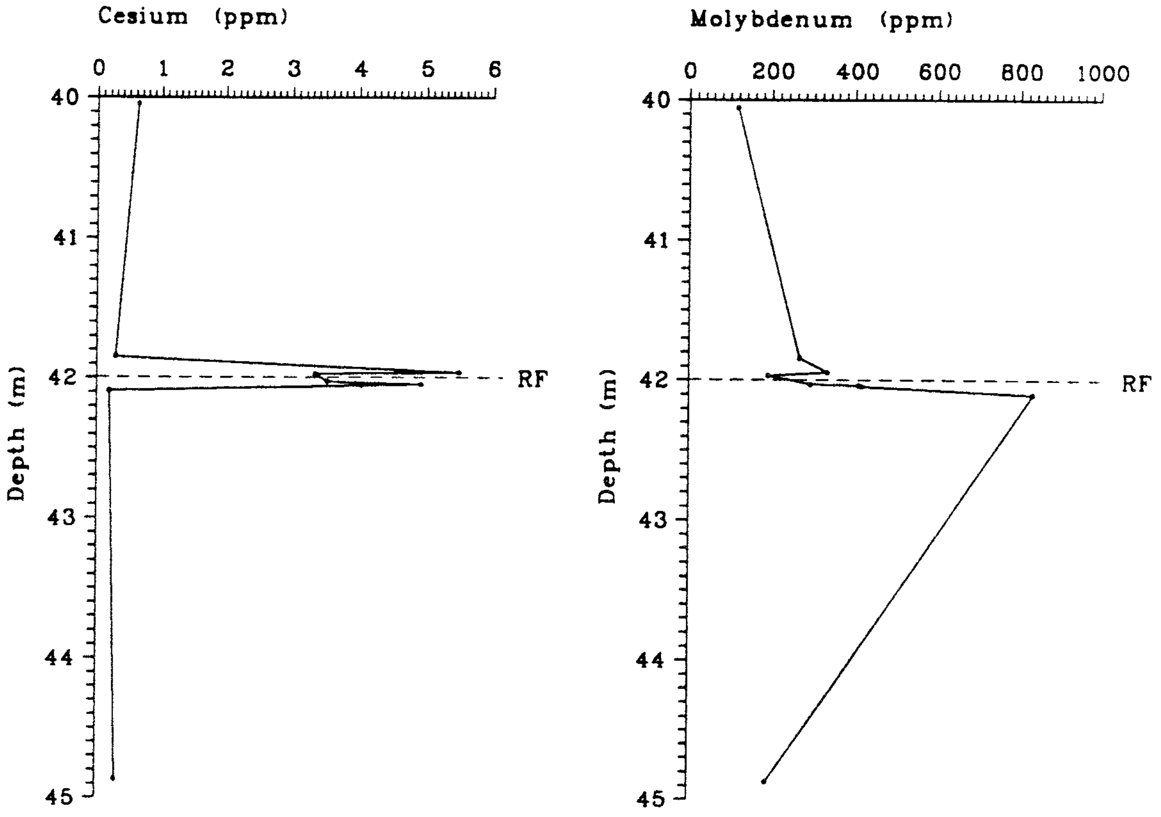

Figure 4.4 Concentration profiles across the 42.0 m redox front in drillcore F1 from the Osamu Utsumi mine (from *[Chapman et al., 1991]*).

4.4 Formation of solid U(VI) phases

At the Alligator Rivers natural analogue site the upper part of the uranium ore consists of uranyl phosphate (saleite). Uranyl silicate is found in a transition zone whereas the deeper parts of the ore consists of pitchblende. The possibility for saleite to form in the near field of a repository has been discussed as one possible solubility-limiting phase for hexavalent uranium. The analysis of the occurrence of saleite at Alligator Rivers includes theoretical modelling aimed at explaining the mechanisms behind the formation of saleite.

The modelling has been performed using a data base for thermodynamic data developed at the John Hopkins University *[Sverjensky, 1990]*. As a starting point for the calculations, that were performed with the EQ3/6 code, an initial water composition was chosen based on samples from one of the bore holes on the site. This initial water composition was saturated with respect to kaolinite, hematite and quartz. The modelling suggested that one way of forming saleite starts with weathering under atmospheric conditions of chlorite, muscovite, quartz, pyrite, graphite, apatite and pitchblende. The sulphide in the pyrite is oxidised to sulphate producing protons, which will keep pH at a level that favours high phosphate concentrations in the groundwater. The high phosphate concentrations favour the formation of saleite in competition with apatite. The oxidising conditions are necessary to keep uranium and iron in their highest state of oxidation.

The modelling efforts have led to the conclusion *[Sverjensky, 1990]* that the saleite formation requires oxic conditions. The unsaturated conditions at the Alligator Rivers site have therefore been interpreted as a key property for saleite formation. This conclusion is in a sense supported by the fact that saleite has not been reported to form at other analogue sites with hexavalent uranium and saturated conditions.

4.5 Radionuclide transport in the near field of a repository

The natural uranium deposit at Cigar Lake in Canada is covered by a clay-rich halo, approximately 3 m thick, in sandstone. The deposit is presently under investigation with an aim to study the release and migration of uranium and other nuclides as an analogue to the near field transport in a repository for radioactive waste *[Liu and Neretnieks, 1992]*. This is carried out by applying similar mass transport models as those used in the performance assessments of repositories to simulate the migration of radionuclides from the ore body.

Hydrogeological modelling and field data show that the sandstone is more permeable than the clay rich halo, the ore body and the basement beneath the ore body, and that there is no hydraulic connection between the sandstone and the other units. Based on these results, transport of uranium from the ore body was modelled as diffusion through the clay-rich halo and subsequent transfer by diffusion into water flowing in the sandstone along the clay-sandstone interface. Further transport in the sandstone was assumed to occur by advection and diffusion. A porous medium model was used, and neither dissolution/precipitation of uranium nor interaction between uranium and solid were considered in the model. Measured uranium concentrations in the water in the ore body was used as source concentration in the calculations, and the water in the sandstone upstream of the ore body was assigned a background concentration of uranium which was based on groundwater analyses. Values of the remaining parameters were selected from results of laboratory and field tests or, in cases where no supporting data were available, assigned values were judged to be reasonable. The conceptual model of the mass transport is schematically depicted in Figure 4.5.

The results of the modelling predicted very low release rates of uranium, about 50 mg/year, and a very small increase in uranium concentration from the background value, about 5 %, in the water in the sandstone adjacent to the clay. Approximately half a metre from the clay sandstone interface

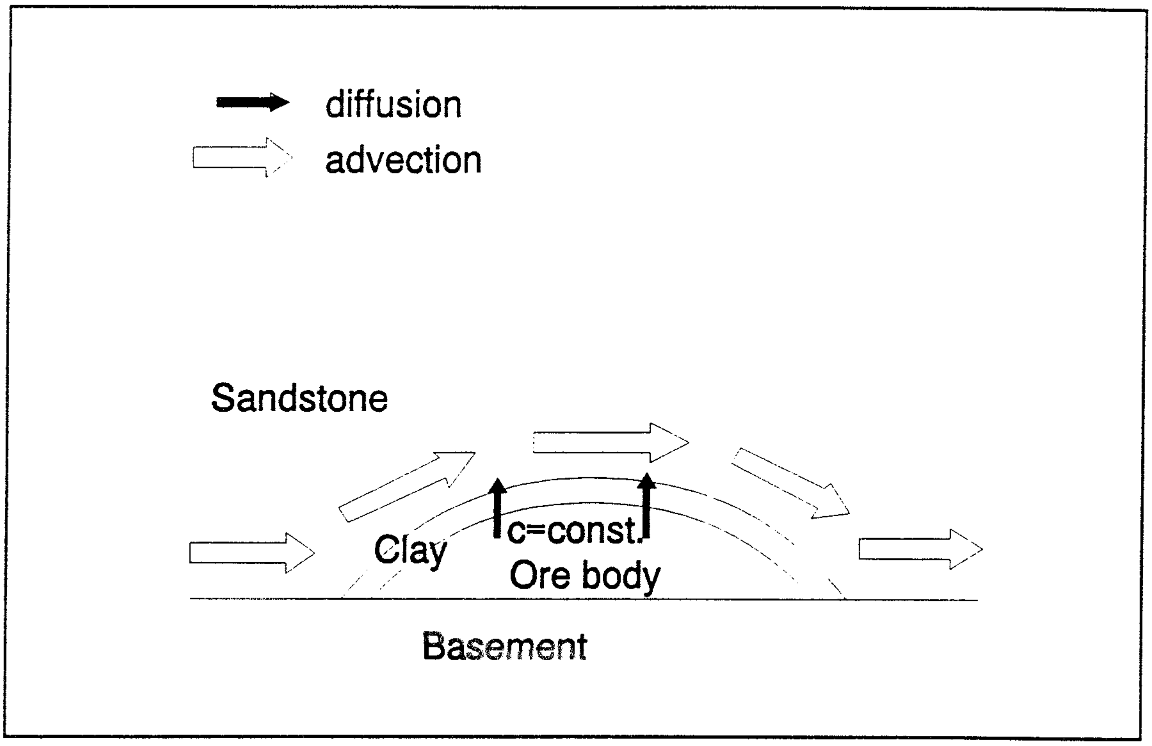

Figure 4.5 Schematic view of the uranium transport modelling at Cigar Lake.

the uranium concentration has declined to the background level. The modelling also showed that the clay layer plays an exceedingly dominant role in retaining dissolved uranium, and that the uranium release rate is much more sensitive to the parameters related to the clay than those of the sandstone.

Field observations support the results of this simplified modelling approach in that no elevated uranium concentrations in the water in the sandstone has been observed. Furthermore, uranium series data indicate that the background concentration in the sandstone surrounding the ore is due to solid uranium of hydrothermal origin, but a slight, recent remobilisation has occurred in the local region of the clay and along some fractures.

The migration of some in-situ produced nuclear reaction products, ^{3}H, ^{14}C and ^{36}Cl from the ore body out through the clay has been studied with a similar model as described above. However, both advection and diffusion through the clay and ore zone are considered. Both a porous media approach and the case of flow in fractures are studied. The model predictions indicated that 98.5 % of the generated ^{3}H is depleted within the ore body by decay, while most of the generated ^{14}C and ^{36}Cl is released from the ore body by groundwater flow and diffusion. Although the release percentage of the latter radionuclides is high, they are still mainly confined within the clay. These results are not contradicted by in-situ measurements which showed elevated concentrations in the ore body but not in the surrounding sandstone. Only small differences were found in the calculated loss of radionuclides by flow between the porous medium model and the fracture model.

A coupled mass transport/chemical equilibrium model was used to simulate mass transport by diffusion and geochemical reactions in the clay zone. Mineral and water compositions observed at the site were used as input to the model. Aqueous species in the ore zone are assumed to migrate by diffusion into the clay and react with both minerals and aqueous species. The oxidising species is assumed to be dissolved oxygen. Predicted pH-values as well as hematite content and total concentrations of iron and uranium in the haematised zone were in agreement with observed values. The time needed for the redox front to propagate 1 m into the clay layer was by the model calculated to be of the order of 10^8 years assuming the present day concentration of dissolved oxygen in the water in the ore zone. A separate calculation of the redox front movement with a "shrinking core" model predicted the corresponding time to be about 10^9 years which is the estimated age of the ore formation.

4.6 Concluding remarks

Many of the phenomena considered to be important in the modelling of radionuclide transport in the near field have been studied in natural analogue studies. As has been demonstrated in this chapter the analogues at Poços de Caldas, Cigar Lake and Oklo all exhibit features that are analogous to the near-field process system. The observations at these sites have served both to demonstrate the existence of different processes under natural conditions and to provide data bases for model validation. Some of the observations, e.g. the extent of enrichment of certain radionuclides at the redox front at the Osamu Utsumi mine, have been unexpected and have thus served to identify processes that need consideration in the near-field modelling. An overview of the support provided by these analogue studies for a near-field model is given below.

The Oklo and Cigar Lake natural analogue studies both support that radiolysis can affect the redox chemistry in the near field. A comparison between the two studies show that an improved understanding both of the production of redox agents and of the transport of these agents within the near field is needed in order to predict the overall effect of the radiolysis. However, hardly Cigar Lake and definitely not Oklo have yet been fully investigated.

The observations at he Osamu Utsumi mine as well as those at the Cigar Lake deposit show that oxidising species can be consumed by ferrous iron as they migrate. At the Osamu Utsumi mine oxygenated water has infiltrated into the rock forming a clearly visible redox front. The source of oxidation at Cigar Lake is probably oxidising substances formed by radiolysis. This supports the general redox-front feature of the near-field model.

In the model many of the redox-sensitive radionuclides are assumed to precipitate as they pass the redox front. This is supported both by the observations at the Osamu Utsumi mine and by observations at Oklo. At the Osamu Utsumi mine concentration profiles of a multitude of elements across the redox fronts indicate that reduction/precipitation as well as scavenging by coprecipitation and sorption takes place. Some of the substances reduced (e.g. UO_2^{2+} and SO_4) are found in the order of centimetres downstream of the front. It has been postulated that the reduction of these species are kinetically controlled.

Some of the elements enriched at the redox front (e.g. Cs) are not recognised as sensitive to redox conditions and are not expected to be precipitated as a result of solubility limitations. The enrichment of these elements are therefore likely to be caused by sorption or coprecipitation with e.g. ferric iron hydroxides. This indicates that there is a potential for interaction between easily soluble radionuclides and corrosion products from the iron canister which should be further investigated and possibly included into the near-field model. The importance of such interaction has recently been assessed *[McKinley et al., 1992]*. The enrichment of trace elements observed at the Osamu Utsumi mine was applied to the near-field conditions assumed in the Kristallin-I analysis. It was found that corrosion products from the steel canister or secondary iron minerals would be capable of immobilising the total inventory of most toxic radionuclides in the waste.

At Oklo some oxidisable fission products have been interpreted to have undergone oxidation due to radiolysis followed by dissolution and migration away from the reactor zone. At a few metres away from the reactor zone they have been reduced and precipitated, probably because the content of oxidising species in the groundwater has decreased.

In the near-field models used both in Finland and in Sweden the main mechanism for radionuclide transport from the canister to the flowing groundwater in the surrounding rock is diffusion through a clay buffer. This type of model is being tested against observations and data from Cigar Lake. Calculations have been made both for uranium and for nuclides formed by nuclear reactions in the ore. In addition, calculations of the propagation of the oxidising zone in the clay were made. These modelling exercises exemplify how assumptions and simplified performance assessment models can be tested on a complex natural system. The results obtained so far are not contradictory to observations at the analogue site which give some support for the applicability of performance assessment models in predicting the behaviour and mass transport in the near field of a repository. Furthermore, the results verify the assumption of a long-term retaining capacity of a clay buffer in a disposal vault in a repository as well as indicating that it may be conservative to assume that the total amount of oxidants produced by radiolysis are available for oxidation of minerals.

5 Radionuclide transport in the far field

5.1 Background

A central part of any performance assessment of a radioactive waste repository is the estimation of the rate of transport of the radionuclides from the repository to the biosphere. This transport takes place through what is called the far field or the geosphere. The transport medium for radionuclides is the groundwater and phenomena such as hydrodynamic dispersion, different types of chemical interactions between radionuclides and the rock, matrix diffusion, channelling, etc, are more or less important. This chapter focusses on attempts to validate different variants of advection/dispersion models using data from natural analogue studies. It is evident that such attempts require the evaluation of the geohydrological system of the site. This evaluation is in this chapter only covered as needed in order to be able to draw conclusions.

The general approach used in model validation attempts is to try to simulate the current spatial distribution of some tracer available in the study area. In several studies this tracer is uranium and the daughter nuclides formed by radioactive decay of uranium. Another tracer that has been used is ferric iron formed by oxidation of ferrous iron. Irrespective of what tracer is used, one major problem encountered in the comparison between measured and computed data is the reconstruction of the historic development leading to the current situation. The models used often assume that today's situation has been prevailing since the onset of the transport process modelled. Isotopic disequilibria and ratios between activities of different radionuclides is one way of age dating the system. In fact, the modelling performed often has the age dating as a primary objective.

In the following sections, some phenomena in radionuclide transport are discussed and a review is made of some attempts at validation of models of the various phenomena. It should be noted that the review is intended to elucidate the extent to which natural analogues have been useful in the validation process rather than to investigate whether specific models are validated or not.

5.2 Advection/dispersion

5.2.1 General

As mentioned in the previous subsection, advective transport with the flowing groundwater is conceived to be the major transport mechanism in far-field radionuclide migration. The dispersion describes the mixing of water moving with different velocities and with different tracer concentrations. The effect of the dispersion is that the moving plume of tracer is smeared so that the edges of the plume becomes "blurred".

All modelling attempts analysed below are based on some form of advection/dispersion model with the addition of various other phenomena. A separate subsection has been devoted to the validation of "conventional" radionuclide transport models. These models are of the type hitherto mostly applied in performance assessments, i.e. models describing advection, dispersion, retardation by sorption equilibrium and radioactive decay.

5.2.2 Analysis

Transport models of the type commonly used in performance assessment of repositories have been used to simulate the radionuclide migration in the weathered zone at the Koongarra uranium deposit in the Alligator Rivers region, Australia. Radionuclide transport modelling carried out within the Alligator Rivers Analogue Project, ARAP, are reported in Volume 14 of the ARAP Final Report series *[Golian and Lever (Editors), 1993]*. *Lever* (in *[Golian and Lever (Editors), 1993]*) applied a simple model which assumed one-dimensional groundwater flow with constant velocity and linear sorption equilibrium between radionuclides in liquid and solid phase. The effects of α-recoil were considered by allowing different members of the same decay chain to have different retardation factors. The model was used to estimate the time over which uranium transport had taken place. This was done based on the observed migration distance and estimates of the groundwater velocity and sorption equilibria (K_d) based on sequential extraction of rock samples as well as by using observed disequilibria between ^{238}U, ^{234}U and ^{230}Th in whole rock samples. The results indicated that uranium migration had occurred for $1 \bullet 10^6$ - $3 \bullet 10^6$ years.

A similar simple one-dimensional model was applied by *Skagius et al* (in *[Golian and Lever (Editors), 1993]*) with the exception that hydrodynamic dispersion was included in the model. The migration time was set to $2 \bullet 10^6$ years and the groundwater flux as well as the K_d-value was assumed to be constant with time, but different values within ranges estimated from groundwater flow simulations and the extent of sorption estimated with the techniques described above were tested. A first set of scooping calculations showed that it was possible to reproduce the observed uranium migration distance as well as the observed uranium concentration level in the solid phase with values of the water flux and K_d in the ranges studied. It was further noted that the shape of the concentration front was better simulated with a dispersion length of 1 m than with one of 10 m (see Figure 5.1). A comparison of calculated and observed activity ratios ($^{234}U/^{238}U$, $^{230}Th/^{234}U$) in solid phase supported the assumption of a migration time of the order of 1 to 2 Million years. It was, however, also concluded that processes of potential importance for the migration were not considered in the modelling, such as weathering of minerals and influence on hydrology due to variations in climatic conditions.

A somewhat more complex model was applied by *Golian* (in *[Golian and Lever (Editors), 1993]*). The weathered zone is assumed to contain two geologically different layers each modelled as one-dimensional transport pipes. One pipe represents the near-surface layer of weathered sandstone and the other represents the weathered schist below the sandstone. The monsoon-like climate in the area causes a dramatic seasonal fluctuation of the water table and change in the lateral flow of groundwater. The fluctuation in the water table is considered in the model by allowing pathways between the two one-dimensional pipes. The effect of weathering is considered by assuming that the rock consists of two phases, a phase which is accessible to flowing groundwater and a phase which is inaccessible. Uranium in the accessible phase is in sorption equilibrium with uranium in the groundwater, but uranium transfer also occurs between accessible and inaccessible solid phase as a result of α-recoil and the weathering sequence. Calculated uranium concentrations in the different phases in each transport pipe were compared with observed concentrations in accessible and inaccessible phases in the weathered sandstone and schist. The preliminary results of the modelling supports the experimental values of the sorption distribution coefficient, K_d, and the independent estimates of groundwater flux Furthermore it was found that the exchange rate of uranium from accessible to inaccessible phase is of the order of the decay constant for ^{234}U and that the migration time is less than 2 Million years.

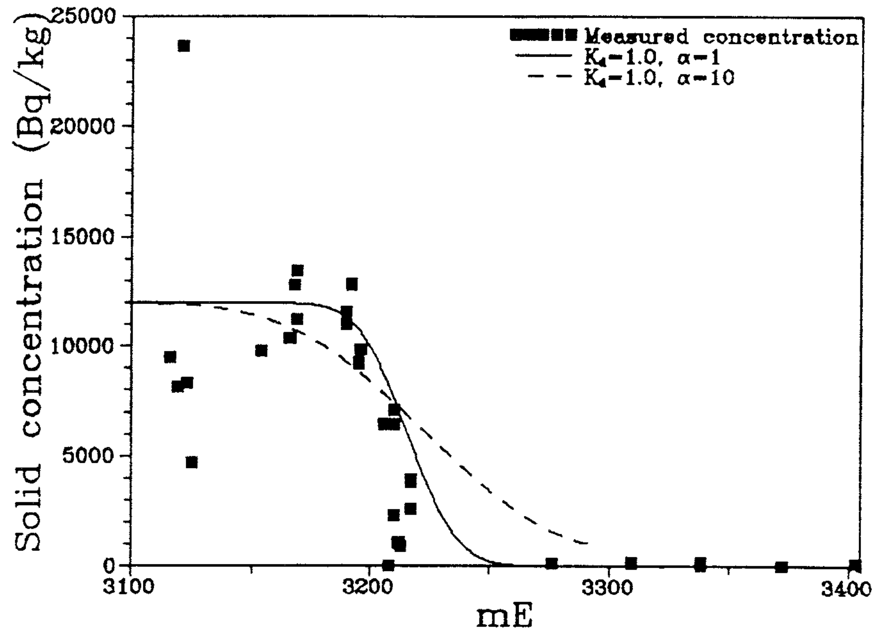

Figure 5.1 Predicted and observed ^{238}U-concentrations at 10-20 m depth in the weathered zone.

In summary it can be concluded that the different modelling attempts seem to give a consistent picture of the migration of uranium in the weathered zone. With K_d-values for uranium of the order of 1 to 10 m^3/kg and a groundwater flux of the order of 1 m/year all models suggest a time-scale of the order of million years for the uranium migration in the weathered zone. However, during these million years the climatic conditions in the area have varied in conjunction with glacial and interglacial periods. It is believed that the climate during glacials was very dry, almost desert-like, with very low water table and almost no groundwater flow, while interglacials involved very heavy rainfalls and high groundwater flow. Possible effects of these variations in groundwater flow still remain to be studied.

The concept of determining the distribution coefficient from measurements of concentrations of natural series radionuclides in the rock and the groundwater (e.g. *[Ivanovich et al., 1988b]*) is intended to circumvent some of the problems with representativeness associated with laboratory measurements of K_d-values. The laboratory measurements are often made on samples of freshly crushed rock despite that it has been shown that old minerals in the vicinity of water conducting fractures play an important role in the sorption process. It is also difficult to show that the water composition used in the laboratory is the same in all respect as the natural groundwaters. Moreover, the small scale of the laboratory measurements has been mentioned as a problem in itself. On the other hand, the in situ approach has been criticised *[Alexander et al., 1990a; McKinley and Alexander, 1991]* on the basis that it cannot distinguish between reversibly adsorbed radionuclides and radionuclides precipitated. The in-situ approach would thus tend to exaggerate the K_d-values compared to conventional laboratory techniques. It is thus very important that the measurements of the concentrations on the solid phase only include the sorbed portion of the radionuclide. It is also important that the water is sampled from a location close to the rock sample being analysed so that the rock/water pair is representative for the sorption process under study.

In the Alligator Rivers analogue Project an attempt was made to differentiate between accessible and inaccessible solid phases. The amount of radionuclides available in the accessible phase was determined by extraction with organic solvents while the total amount of uranium was determined by total dissolution of the rock sample. It was found that 25-60 % of the total uranium content is present in the accessible phase *[Golian and Lever (Editors), 1992]*. In the Alligator Rivers Analogue Project the range of K_d -values recommended is 0.5-2 m^3/kg for the accessible phase.

It is obvious that the use of in-situ derived data on sorption or retardation requires a good knowledge of the sorption mechanisms and the studied geochemical system. This also puts requirements on the employed experimental techniques that have to be designed to be selective and to study only the phenomena of interest.

5.2.3 Conclusions

Three attempts to simulate the present uranium distribution in the weathered zone at the Koongarra ore deposit have been reviewed. All three models give a consistent picture of the time (1-3 million years) during which the present situation has developed. The assumptions used in the modelling are, however, greatly simplified. The groundwater hydrology has been assumed to be constant despite that the climate may have varied between desert-like conditions and the present monsoon situation.

The modelling performed to date has been used mainly to interpret the development of the site. There is still a lack of independent information about the initial conditions and the variation of the boundary conditions during the modelled period. This lack of information on initial and boundary conditions is probably typical for the study of far-field natural analogues making it difficult to use the analogues for validation of large-scale transport models. The interpretative modelling exercises are, however, valuable for the general understanding of processes and the justification of assumptions used.

5.3 Matrix diffusion

5.3.1 General

In fractured rock, radionuclides released from the near-field of a repository will be transported towards the biosphere with groundwater flowing in fractures in the rock. Besides fractures, the rock contains microfractures and pores with effectively stagnant groundwater. Under naturally prevailing hydraulic gradients transport of dissolved species by flow in these microfracture and pore systems can be neglected. However, migration of dissolved species in microfractures and pores in the rock matrix may take place by diffusion. This means that matrix diffusion can act as a retarding and diluting mechanism by removing radionuclides from the groundwater flowing in the fractures and enlarging the rock surface accessible to sorption of radionuclides *[Neretnieks, 1980]*.

The importance of matrix diffusion as a retardation mechanism is largely dependent on the porosity of the rock matrix adjacent to the fracture and on the connectivity of the pore system in the matrix of the rock as well as on the area of the fracture surface in contact with the flowing groundwater.

The matrix diffusion phenomena has been extensively studied in the laboratory scale (e.g. *[Bradbury and Green, 1985; Bradbury and Stephen, 1986; Skagius and Neretnieks, 1986a; 1986b; 1988; Kumpulainen and Uusheimo, 1989]*). Results from these experiments confirm the existence of connected pores in rock and fracture filling materials (cm-scale) through which diffusion of solutes occurs. The weaknesses with laboratory experiments are the potential change in rock porosity of the de-stressed samples as well as the small space and time scale over which the diffusion mechanism can be studied. Although observations in man-made field experiments, (e.g. *[Birgersson and Neretnieks, 1990; Frick et al., 1991]*) support the laboratory scale findings, they cannot give evidence for matrix diffusion over time periods relevant for repository safety. Here, studies of natural systems which have been active over geological time-scales play an important role.

There are many potential natural systems which may be used to show that there exists an interconnected pore system in the matrix of the rock and that this pore system is accessible to species carried by groundwater flowing in fractures. Examples of such systems are: remobilisation and transport of naturally occurring uranium in rock adjacent to water-bearing fractures, rock adjacent to fractures in which the groundwater has changed from saline to fresh, and the interaction between species, such as oxygen, in the groundwater in fractures and the fracture surface with a resulting reaction front propagating into the rock matrix.

5.3.2 Analysis

One way to seek evidence for matrix diffusion is to study the behaviour of natural tracers in rock. A redistribution of natural elements in rock adjacent to a water conducting fracture, or the spreading of radionuclides in unfractured rock surrounding uranium deposits are examples which qualitatively may indicate that there exists interconnected pores in the rock matrix in which transport of natural elements may have occurred by diffusion over time-scales of interest in performance assessment.

Ideally, an exponential concentration profile of the tracer in the rock adjacent to the fracture or the uranium deposit should prevail. However, this requires that no changes have taken place in hydraulic, geologic, thermal, etc conditions over the very long times the system has been active. This is not to be expected, and the difficulty in defining the various conditions and the actual time-scale for the analogue reduces the possibility to quantitatively verify diffusivities measured in laboratory or field experiments.

To be able to verify matrix diffusion in natural systems, either qualitatively or quantitatively, a thorough understanding of the system studied is needed. An observed concentration profile of a tracer in rock may be the result of a chain of several processes occurring in series or parallel to each other. Furthermore, the duration of the processes may have varied over the long time of interest.

Below, some examples are given of natural analogue studies that have been carried out with the aim to investigate matrix diffusion. In these studies, the concentration of various elements around a source or sink has been studied to determine if, and over which distance, redistribution of the elements have occurred. In some cases an attempt has been made to quantitatively estimate diffusivities from observed concentration profiles.

Qualitative indications of matrix diffusion

Crystalline rock cores, two from the Grimsel underground laboratory in Switzerland, one from the NAGRA exploratory borehole at Böttstein in Switzerland and one from the SKB pilot borehole at Kråkemåla in Sweden, which intersected water-conducting fractures have been analysed for a number of elements *[Smellie et al., 1986; Alexander et al., 1990a]*. On microscopic investigation, all four samples showed extensive and interconnected porosity.

The drillcores from Grimsel showed no clear concentration gradients of uranium or thorium, but based on measured activity ratios il was suggested that radium mobilisation had occurred in one of the cores to a depth of about 3 cm from the fracture surface and that re-mobilisation of uranium had taken place in the other core to a depth of 10-20 cm from the fracture surface. Both cores were found to be altered, but hydrothermal alteration was generally more pervasive in the latter core while the former had undergone low-temperature brittle shearing.

The Böttstein core was composed of pegmatite and granite, with the fracture located in the pegmatite and the contact between pegmatite and granite about 6 cm from the fracture surface. Hydrothermal alteration of the granite extended for about 8 cm from the pegmatite contact. Also in the Böttstein core, indications mobilisation of uranium and rare earth elements over distances of the order of 10-20 cm from the fracture surfaces were found.

The Kråkemåla sample is a weakly altered granite. A clear increase in uranium content as well as an accumulation of ^{234}U relative to ^{238}U in the vicinity of the fracture were observed, while the rest of the core showed a depletion of both ^{234}U and ^{230}Th relative to ^{238}U. This was suggested as being the result of accumulation in the granite marginal to the fracture of uranium leached from the granite indicating uranium transport over at least 40 cm. An alternative explanation given was that the uranium accumulation is the result of deposition of uranium transported by water within the fracture, implying uranium penetration of the order of 3 cm into the rock matrix. Fission track analysis showed that the uranium profile in this 3 cm wide margin adjacent to the fracture corresponded with the dispersion of Fe-oxyhydroxides and alteration products.

Results from a study of a section of rock extending from a single, water-conducting fracture, in an oxidising groundwater environment into the granite of the Kamlunge test site in northern Sweden are presented by *[Smellie et al., 1993]*. Thin section studies indicated that hydrothermal alteration has affected the rock in a zone of some 2 to 3 cm adjacent to the fracture resulting in increased uranium and thorium concentrations. Loss of uranium over times of the order of 10^5 years, probably under reducing conditions, has affected the complete section of the rock, indicating the existence of interconnected porosity over at least 7 cm. Natural decay series data together with Mössbauer Spectroscopy and $\delta^{18}O$ measurements reveal more recent, rapid oxidation and removal of uranium, with the zone of oxidation extending about 3 to 4 cm into the rock from the fracture.

Within the Palmottu Analogue Project, the distribution of uranium series nuclides in two rock cores intersecting natural fractures was investigated *[Suksi and Ruskeeniemi, 1991; Suksi and Ruskeeniemi, 1992]*. In both samples, uranium was found to be enriched in a limited alteration zone near the fracture surface. α-particle radiography showed that the density of α-activity decreased rapidly with distance and was associated with alteration products (Fe-oxyhydroxides and clays). In one of the samples the decrease was almost exponentially over a distance of about 2.5 cm from the fracture surface into the rock. A clear correlation between α-activity and microfractures could also be seen in this sample. In the other sample, α-activity was concentrated near the grain boundaries and an elevated activity level was still visible at least 8 cm from the fracture surface. Uranium series data indicate that the disturbance affecting this latter core may have occurred considerably earlier than that of the former core. Selective extraction showed that most of the uranium occurred loosely bound to the alteration products, in both samples.

Results from another study of element mobility in a crystalline rock core located between two open fractures only a few metres away from the uranium mineralisation at Palmottu are reported by *[Kumpulainen et al., 1992]*. A multitude of elements were analysed and the element profiles showed significant alteration extending about 2.5 cm into the rock from one of the fracture surfaces. The other fracture surface showed only very slight alteration. Analyses of uranium and thorium concentrations showed an enrichment of uranium to a depth of about 3 cm from the altered fracture surface and a region depleted of uranium extending for about 20 cm into the parent rock. In the vicinity of the slightly altered fracture, no uranium mobilisation was observed.

Also *[Montoto et al., 1992]* conclude that a zone of enhanced element mobility exists close to hydraulically active fractures. They report, based on studies of samples from El Berrocal, Stripa and Whiteshell, that the zone of enhanced mobility extends between 35 and 80 mm from the fracture into the rock. The zone of mobility was associated with microstructural changes related to weathering around the active fracture, and the evidence of diffusion was limited to the altered zone or to part of it.

The mobilisation of radionuclides in a piece of drillcore intersecting a calcite-filled fracture at the Jabiluka uranium deposit in the Alligator Rivers Region in Australia has been investigated by *[Nightingale, 1988]*. The core was composed mainly of quartz-chlorite-mica schist with no visible sign of weathering. Uranium series data showed that the fracture surface had the highest concentration of uranium and that groundwater had influenced the surrounding rock within a few cm of the fracture.

Rock samples from the Koongarra uranium deposit in the Alligator Rivers Region, Australia, have been studied with the aim to investigate the degree to which uranium has migrated from water-conducting fissures into the rock matrix *[Edis, 1992]* Very little penetration of uranium was observed into the unaltered rock while a significant amount was present in the secondary fissure coating material. The α-activity away from fissures into unfractured, unweathered and unaltered quartz-chlorite rock matrix decreased exponentially to a distance of about 180 μm from the fissure. Penetration of uranium appeared to increase with the degree of alteration and weathering, reflected in an observed concentration profile extending a few mm into a sample of weathered quartz-chlorite schist.

[Shea, 1984] studied the movement of ^{235}U from a hydrothermal deposit into the enclosing granitoid country rock by the fission track method. In two samples, measured concentration gradients extended approximately 5 and 1 cm, respectively, away from a uranium vein and veinlet, and two other samples showed limited movement (about 1 to 3 mm) along a few microcracks. Three samples showed no evidence of uranium movement.

Non-fractured core-sections between pairs of water conducting fractures at the island of Hästholmen, Finland have been investigated for concentration profiles of chloride and sulphate

[Valkiainen, 1992]. As a result of post-glacial land uplift and infiltrating rainwater, the groundwater flowing in fractures in the rock has changed from saline to fresh. The results showed a depletion of saline water from the rock matrix in contact with the water-conducting fractures suggesting interconnected porosity in the scale of metres.

Quantitative estimates of diffusivity

An attempt to estimate diffusivities from measured concentration profiles has been made by *[Shea,1984]*. By matching the observed concentration profiles for chlorite grains to theoretical curves calculated by a diffusion model, values of the apparent diffusivity, D_a in the range 10^{-21} to 10^{-18} m²/s were obtained. For concentration curves observed in the solid rock matrix estimated Da-values ranged from 10^{-19} to 10^{-16} m²/s. The model applied is very simple in that it assumes constant conditions over the time of interest, which in the above studies are of the order of 10^4 to 10^7 years *[Shea, 1984]*.

Apparent uranium diffusivities in the range of 10^{-10} m²/s can be obtained based on data in *[Smellie et al. 1986; Alexander et al., 1990a]* for bulk rock close to fractures and pegmatitic veins. It should be noted that the apparent diffusivity is dependent on the magnitude of the sorption. It is therefore important that the estimation of the diffusivity is combined with an analysis of the geochemical situation and an evaluation of the sorption properties. For sorption, such as that occurring for hexavalent uranium in certain environments, the apparent diffusivity approaches the diffusivity in the pores.

The chloride concentration profiles observed in granitic rock at the island of Hästholmen in Finland were compared with theoretical curves calculated with a diffusion model *[Valkiainen, 1992]*. The best fit was obtained with an apparent diffusion coefficient of $2 \bullet 10^{-9}$ m²/s, which corresponds to an effective diffusion coefficient of $1 \bullet 10^{-12}$ m²/s. This value is about an order of magnitude higher than the effective diffusivity measured in the laboratory. Suggested explanations to the discrepancy were: the occurrence of additional microfractures in the larger scale, the existence of a vertical water-conducting fracture near the sampling location and/or the use of a one-dimensional diffusion model which may be inappropriate *[Valkiainen, 1992]*.

In the recent safety analysis of a repository according to the KBS-3 concept an apparent diffusivity of $1.9 \bullet 10^{-17}$ m²/s was applied for uranium under reducing conditions ($D_e = 10^{-13}$ m²/s, $K_d = 2$ m³/kg) *[SKB, 1992a]*. This value, which was selected from laboratory measurements of the effective diffusivity, D_e, and sorption of uranium, falls in the range of D_a-values for uranium in a granitoid rock matrix as estimated by *[Shea, 1984]*. Another quantitative analysis of the results from the analogue studies can be made by comparing the observed distances of uranium movement with distances calculated with a diffusion model. Assuming constant conditions over the time of interest, the depth of movement by diffusion of a tracer from a constant source can be expressed as (e.g. *[Neretnieks, 1980]*)

$$\eta_{0.01} = 4 \sqrt{D_a t}$$

where $\eta_{0.01}$ is the distance from the surface where the concentration is 1% of the concentration at the surface at time t, and D_a is the apparent diffusivity.

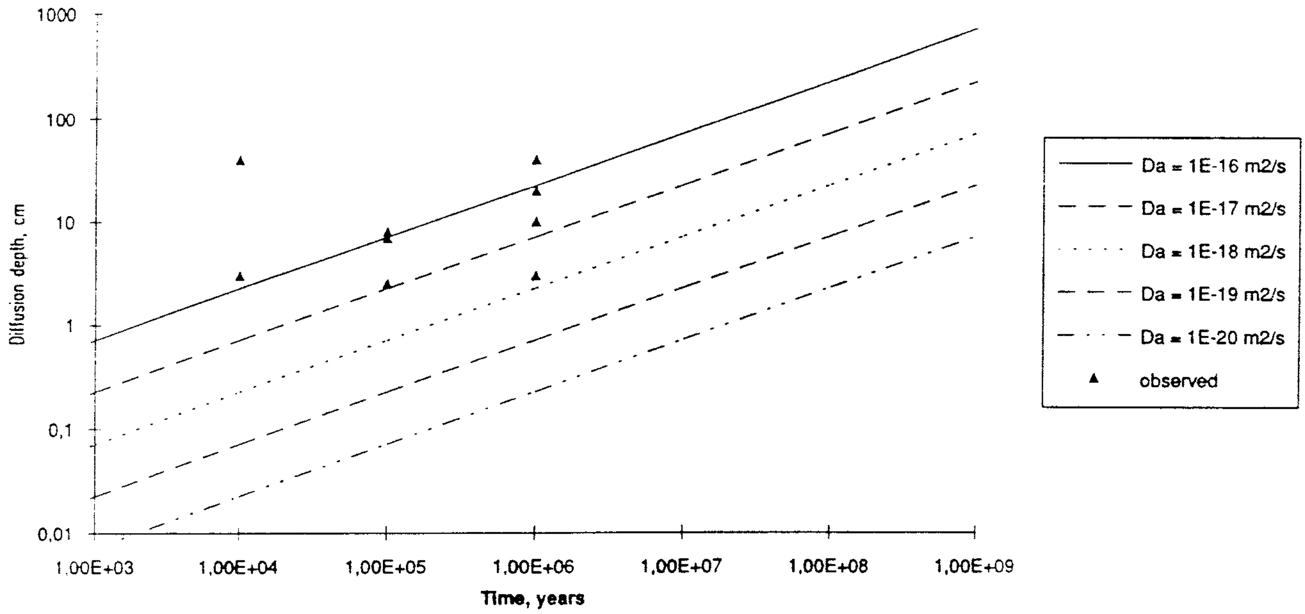

Figure 5.2 Calculated diffusion depths versus time and observed depths versus estimated times of movement in rock samples from Finland (Palmottu), Sweden (Kamlunge, Kråkemåla) and Switzerland (Grimsel).

Calculated diffusion depths, $\eta_{0.01}$, as a function of time are shown in Figure 5.2 in logarithmic scales for different values of the apparent diffusivity. In some of the analogue studies, an estimated time for the observed depth of uranium movement is reported. These results for crystalline rock are also depicted in the figure. However, it must be remembered that both the observed depths of movement and the corresponding estimates of time are very uncertain. Furthermore, the time-scale and thereby also the penetration distances observed are inherently limited by the half-lives of the natural series nuclides *[Alexander et al., 1990a]*.

Comparing the observations with the results from the diffusion model indicates apparent diffusivities of the order of 10^{-18} to 10^{-16} m^2/s. To some extent this supports the apparent diffusivity of $1.9 \bullet 10^{-17}$ m^2/s used for uranium in the SKB 91-study *[SKB, 1992a]*.

5.3.3 Conclusions

The majority of the results from the analogue studies of matrix diffusion of uranium, qualitatively indicate the presence of a connected porosity extending of the order of cm to tens of cm from a fracture surface into the rock matrix. Furthermore, the combination of observed penetration depths of uranium and estimated time-scale are in good agreement with predictions with a simple diffusion model using apparent diffusivities based on laboratory measurements. The uncertainties in the assumption of a continuous process and constant conditions over time-scales of 10^4 to 10^6 years, as well as in the estimates of this time-scale are, however, large. Alternating uranium leaching and deposition may have occurred as a consequence of changes in conditions, but the observations suggest that the apparent diffusivity of uranium is at least of the order of 10^{-18} m^2/s.

The results also indicate that the degree of alteration of the rock may be of importance to uranium movement. Most of the rock samples in the referenced studies were found to have undergone some degree of alteration whether it be hydrothermal alteration, shearing, decompression, etc. The observed depth of uranium movement was considerably greater the more altered samples. There are several possible explanations to this. Firstly, the alteration creates an increased porosity in the altered zone thus enhancing the diffusivity. Secondly, the altered fracture surfaces are not redox active. This means that the probability for coprecipitation on the altered fracture surfaces is smaller than on fresher surfaces. Thirdly, it is difficult to avoid damage on the surfaces when sampling the rock. It is therefore possible that the most shallow penetration depths cannot be observed.

Another issue that was identified as potentially important to matrix diffusion in Palmottu, Finland, is the type of fracture conducting the groundwater *[Suksi and Ruskeeniemi, 1992]*. No evidence for matrix diffusion was found in samples with shear fractures as opposed to samples with fractures opened in a tensile stress field. This was suggested as being due to a sealing of the pores in the rock matrix close to the fracture by secondary minerals formed during shearing. Although site-specific investigations are needed to finally evaluate the potential for matrix diffusion at a repository site, generic studies could still be worthwhile in order to further examine the role of alteration and fracture forming mechanisms for matrix diffusion. At Grimsel, however, there are signs that the matrix diffusion is more extensive in tensile fractures *[Alexander et al., 1990a]*.

Most of the natural analogue studies of matrix diffusion are confined to investigation of potential movement of the uranium series radionuclides which to a large extent interact with the rock minerals. To be able to evaluate observed concentration gradients and disequilibria data the processes involved in the fixation on the rock have to be considered in the interpretation, in addition to matrix diffusion. This requires a broad and thorough understanding of the present and past conditions at the site. Furthermore, the tracer-rock interaction largely decreases the rate of movement and the distance over which movement is observed may be much less than the actual scale of interconnected porosity. This is to some extent supported by the results from the study of salinity profiles in rock from Hästholmen, Finland *[Valkiainen, 1992]*. More such studies of natural systems involving inert tracers would be helpful to give further evidence for interconnected porosity in larger parts of the rock matrix.

5.4 Channelling

5.4.1 General

Groundwater flow has been observed to be very unevenly distributed in many types of geological media. The flow preferentially takes place along more pervious structures sometimes referred to as preferential pathways or channels. Observations, both from man-made experiments *[Abelin et al., 1987; Birgersson et al., 1992]* and from mapping of different excavated facilities *[Palmquist and Lindström, 1991; Neretnieks, 1987]*, show that different fractures carry very different amounts of water and that a significant portion of the fractures are essentially dry. There is also evidence that the water flow is unevenly distributed within a fracture plane and that only a portion of the fracture is hydraulically active *[Abelin et al., 1990]*. The uneven distribution of flow between fractures as well as within a fracture is often collected under the term channelling.

Channelling affects radionuclide migration by widening the distribution of migration velocities and by reducing the contact area between the flowing groundwater and the rock. The effect of widening the velocity distribution is that a portion of the migrating radionuclide plume will arrive at the recipient much earlier than the average travel time. For radionuclides with a travel time that is greater than the radioactive half life, channelling would increase the release rate to the recipient. On the other hand, the release rates will be lowered for long-lived radionuclides with a travel time that is greater than the duration of the release from the near field. The reduction of contact area between rock and flowing groundwater will result in a reduction of the sorption and will hence increase the migration velocity. These effects have been discussed and accounted for in the SKB-91 study *[SKB, 1992a, Elert et al., 1992]*.

The observations referred to above are observations of current flow patterns in geological structures that have been severely disturbed by excavation work. It therefore cannot be ruled out that the observed flow patterns have been corrupted by the disturbance. Studies of natural analogues could potentially provide a demonstration of the channelling phenomenon under conditions that have been undisturbed. One would then e.g. look for a natural tracer (chemical. mineralogical, etc.) that has moved along channels and that could be recorded today. Such measurements would also be of great value to support the validation of models describing channelling.

5.4.2 Analysis

The data from the Poços de Caldas natural analogue study have been analysed by applying the channelling concept *[Romero et al., 1990]* on a large (100s of metres) scale. The redox front observed at the Osamu Utsumi open pit uranium mine at Poços de Caldas has been estimated to evolve during the last 70-90 million years, while the mine has been in operation since 1975. Compared to the rate of the development of the redox front the mining period is very short. It can thus be assumed that the present redox front has developed under essentially natural flow conditions. The fact that a tracer can be observed that have moved during a long period of time under natural conditions makes the use of the data from the Osamu Utsumi mine potentially valuable as for model testing as the data have not been corrupted by human intervention such as drilling and tunnelling.

The model concept used in *[Romero et al., 1990]* is illustrated in Figure 5.3. Oxygenated water infiltrates into a fracture or channel at the ground surface. As the water moves down the channel oxygen diffuses sideways into the matrix. At the beginning of the process the channels are completely independent of each other, Figure 5.3b. After a certain critical time the oxidised rock associated with adjacent channels have grown together to form a continuous oxidised zone at the surface, Figure 5.3c. The mathematical expression for the rate of movement of the redox finger changes at this critical time.

The process was modelled with five different assumptions regarding channel geometry and boundary conditions:

- Channelling in planar channels (slabs) assuming constant flow rate· Channelling in cylindrical channels assuming constant flow rate
- Channelling in cylindrical channels assuming constant flow rate and that the ground surface is eroded at a constant rate
- Channelling in cylindrical channels assuming that the inlet flow rate is changed every 1 000 years and that the surface is eroded at a constant rate
- Channelling in cylindrical channels assuming that the inlet flow rate changes every time the peak of the redox front has advanced a further 100 m

The modelling was subject to large uncertainties as no site-specific data on the distribution of channels and flow rates in the channels existed. In the absence of such data, data extrapolated from observations in the Swedish SFR-plant for disposal of low and intermediate-level waste were used.

The first two models that assumed constant infiltration rate and no erosion yielded penetration depths of the redox fingers that were many kilometres compared to the observed depths in the order of 100 m. It was argued that several of the model assumptions were unreasonable.

The penetration depths obtained from the third model applying an estimated erosion rate of 50 m per 1 million years were in the order of 20-200 m for the smallest channels whereas the depth for large channels tended towards very large values. Two possible reasons for the large penetrations depths were identified; i) the channels were assumed to extend infinitely downwards whereas in reality the channels could be expected to maintain their identity for tens to hundreds of metres only as they will form a network on that scale and ii) the flow rate was assumed to be constant along the whole length of the fracture when it in reality might be expected to decrease with depth, e.g. due to decreasing hydraulic gradients and increasing rock stresses leading to decreased permeability.

The rationale for varying the flow rate in the last two models were to account for the change of conditions at the inlet of the channel caused by the erosion. The penetration depths obtained from the fourth model assuming change of flow rate at regular time intervals were much greater (in the order of several kilometres) than the observed depths. This was explained by the fact that the propagation of the front in this concept will be largely governed by the periods with high infiltration rate, during which erosion will be of little significance.

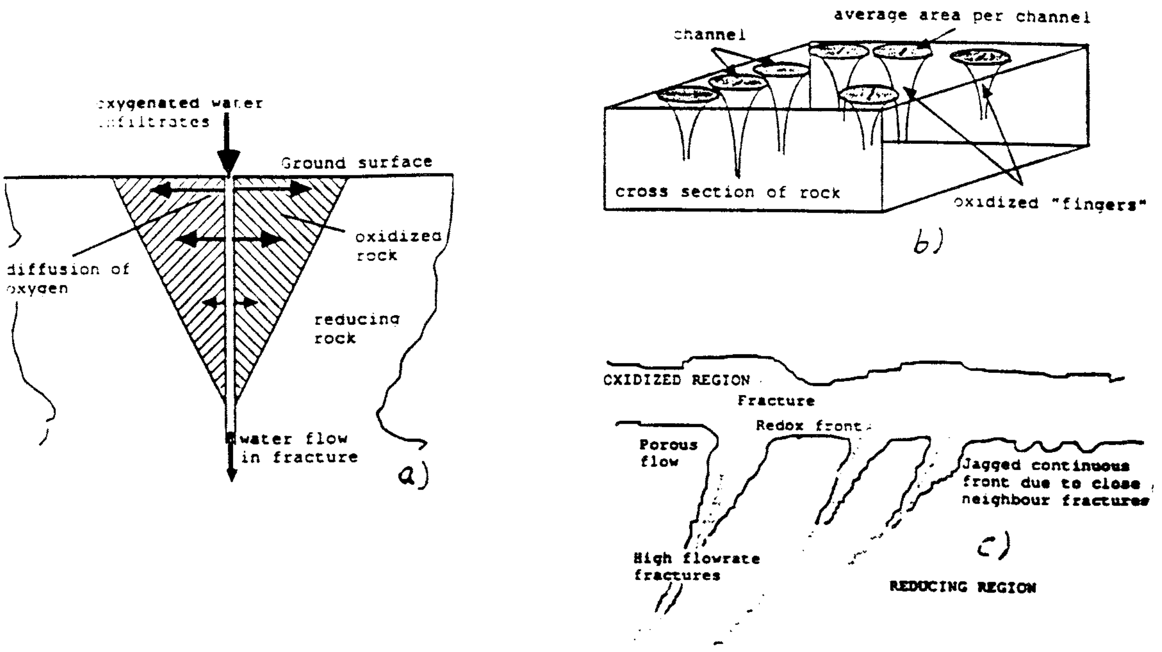

Figure 5.3 Sketch of the conceptual model used to simulate the movement of the redox front at Poços de Caldas showing a) the physics of the model, b) the geometry of the initially independent channels and c) channels that have grown together by sideways diffusion of oxygen (from *[Romero et al., 1990]*).

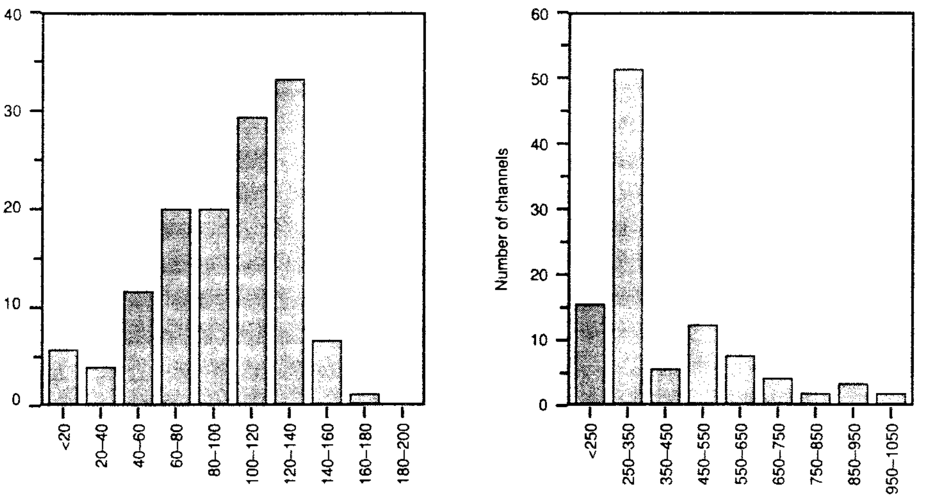

Figure 5.4 Statistics of observed (left) and modelled (right) penetration depths of redox fingers at Poços de Caldas. A model assuming variable infiltration rate and constant erosion rate was used. (From *[Romero et al., 1990]*).

The statistics of the penetration depths from the fifth model were in better agreement with the observed pattern. The observed and calculated depths are shown in Figure 5.4. When the penetration depth is used as a criterion for changing the flow rate, as in model five, the proportion of the time with slow advancement of the front, and hence a large influence of erosion, will be large. This means that the penetration depths will be correspondingly smaller.

Although the basic data used are associated with large uncertainties, and that therefore the number of undetermined parameters is so large that the value of the exercise from a validation point of view is reduced, the importance of certain parameters such as the distribution of flow rate, networking of channels, etc has been demonstrated. The data from Poços de Caldas have a particular value because of the availability of an easily detectable tracer that has moved along identifiable hydraulic paths for a long period of time. They do, however, not shed any light on the distribution of flow within a fracture or a fracture zone.

Observations e.g. of staining of fracture surfaces by coloured minerals such as haematite could potentially contribute to elucidating this issue. It appears, however, that such data has not been extensively analysed in terms of quantification of channelling. Instead, pumping tests and man-made tracer experiments have been used, see e.g. *[Bourke, 1987; Abelin et al., 1990]*. Man-made experiments are mostly carried out at increased water pressures, enhanced hydraulic gradients or some other unnatural stress on the system. Such stresses tend to open up other flow paths than those that would have been open under natural conditions. Furthermore, drilling, sampling and tunnelling always affect the rock by changing the natural stress field so that the geometry and nature of the flow paths change. There is thus a potential which has not yet been fully utilised that observations of natural tracers such as those mentioned above could contribute significantly to the understanding of radionuclide transport.

5.4.2 Conclusions

Channelling is a phenomenon that affects both the distribution of groundwater flow rate between different pathways and the contact area between the flowing water and the rock surfaces and should thus be considered in performance assessments. Channelling has been and is studied extensively in man-made experiments and in theoretical studies. It appears, however, that only very few attempts have been made to analyse natural tracers with the objective to quantify channelling. The analysis of the large-scale channelling at Poços de Caldas referred to in the previous section was primarily aimed at describing the movement of the redox front and not to quantify the movement in terms of channelling. It was clearly demonstrated that uncertainties about the historical development of the redox front and about the boundary conditions severely affected the possibilities to draw quantitative conclusions regarding the channelling properties at the site. The analysis has, however, been of value as a demonstration of the effect of certain assumptions.

5.5 Coupled geochemical transport modelling

5.5.1 General

The standard type of radionuclide transport models utilised to date in performance assessments account for the chemical conditions in the groundwater through some type of retardation factor calculated from distribution coefficients, K_d-values. Some of these models use a non-linear sorption isotherm accounting for the fact that the distribution coefficient can decrease as the concentration in the groundwater increases. Both these approaches are purely empirical and the distribution coefficients are often strongly dependent on the chemical and mineralogical environment.

During the last decade a family of transport models accounting for the thermodynamics of chemical equilibria has been developed. These models, in addition to transport, calculate also the speciation and solubility of the radionuclides using basic thermodynamic theory and data. Two types of such models exist. In the first type, the fully coupled models, a differential equation is set up for each of the species being transported. The transport equations are then coupled through the laws of chemical equilibria. This approach results in a system of coupled partial differential equations with one equation for each specie transported. To take account of the complexity of the chemical system, the number of differential equations to be solved simultaneously often becomes very large requiring significant computer capacity for the solution.
The second type of model is based on iteration between a conventional transport model and thermodynamic equilibrium model. The speciation is calculated at each time step and for each grid point in the spatial discretisation by calling a subprogram doing the speciation calculation. The computational effort required in this type of model is often significantly less than for fully coupled models.

Due the complexity of the coupled geochemical transport models they have yet mostly been applied to resolve research issues. The codes generally only allow application to one-dimensional problems. Some of the codes also have problems to represent certain types of chemical systems such as redox reactions and sharp chemical gradients, e.g. redox fronts. Several codes have been applied to natural analogues and the experience from such exercises have contributed to the initiation further model development.

5.5.2 Analysis

The redox front system at the Osamu Utsumi mine has been simulated with two coupled geochemical transport codes namely CHEQMATE and CHEMTARD *[Cross et al., 1991a; Chapman (Ed.), 1992]*.

The CHEMTARD code is a fully coupled code. The main objective of the CHEMTARD-modelling was to simulate the processes involved in the uranium transport across the redox front. The conceptual model included conversion of pyrite to iron oxyhydroxides by infiltration of oxygenated water, dissolution of pitchblende ore followed by release of hexavalent uranium species to the groundwater, sorption of hydroxy and carbonate species of hexavalent uranium onto iron oxides and diffusion and reduction of uranium across the redox front with the formation of secondary pitchblende ore. In agreement with the observations at the site the results of the calculations show that the amount of uranium that is associated with iron oxyhydroxides in the oxidised upper part of the rock is significant compared with the amounts precipitated on reducing side of the front. This indicates that there may be a higher potential for retention around an iron canister than has so far been realised (see also Section 4.6).

The simulated rate of movement of the redox front is considered reasonable. The model has, however, failed to simulate the formation of secondary pyrite which is associated with the pitchblende nodules on the reducing side of the front.

The CHEQMATE code solves one-dimensional diffusion, electromigration, advection and dispersion. The chemical equilibria are iteratively coupled to the transport part. The objective of the CHEQMATE-modelling was to simulate processes governing the proliferation of the redox front. The conceptual model included similar processes as those included in the CHEMTARD model but had a stronger emphasis on mineral conversions. The modelling results show some encouraging agreement with field data. These include the approximate rate of migration of the redox front, the sharp redox transition at the front, certain mineral transformations, and concentrations of various aqueous species in the system. Some aspects of the system were, however, not as well simulated. This included for example the uranium concentration on the reducing side of the redox front which was predicted to be lower than the measured data. Also, the model failed to simulate the formation of secondary pyrite. The low uranium concentration on the reducing side was interpreted as a consequence of the model predicting highly crystalline uraninite as solubility limiting phase instead of the more soluble low-temperature form, pitchblende, that characterises the site. The difficulties to calculate correct pH-values in the first modelling attempts led to corrections of the data base HATCHES used by the CHEQMATE code *[Cross et al., 1991b]*.

5.5.3 Conclusions

This type of models is considerably more complex than conventional transport models. From the application reviewed in this report it is evident that the application of coupled geochemical transport codes requires substantial insight into the characteristics of the geochemical system. It was possible to properly simulate several of the main characteristics of the redox-front system at the Osamu Utsumi mine whereas some aspects were poorly described by the model. Plausible explanations could be given to all the identified deviations that were found to derive from deficiencies in the thermodynamic data used and on possible crosscontamination in the groundwater sampling procedure.

5.6 Transport of radionuclides with colloids

5.6.1 General

The radionuclide transport models used in previous performance assessments (e.g. by SKB) are based on the radionuclides' solution chemistry and assume that the radionuclides are transported as dissolved species. Groundwater may, however, transport material in the form of particulates. The particle sizes can cover a wide range. In addition, the composition of the particles can vary as their origin can be e.g. eroded geological material, or material that has precipitated from the groundwater due to differences in chemical environment between different locations.

Colloids in the groundwater can be significant for the performance of a repository in two ways. Firstly the surfaces of the colloids are potentially more reactive than mineral surfaces in general due to high surface/volume ratio and to the fact that surfaces of colloids often are associated with a negative electrical charge that attracts ionic species of the opposite charge. If the reactive character of the colloids are neglected in the assessment of the hydrogeochemical system spurious results could emerge from the analysis.

Secondly, radionuclides could be sorbed onto the colloids and be transported both by advection and diffusion through the geological barriers. Theoretically the radionuclides themselves could be precipitated and form colloids in the groundwater. Radionuclide transport with colloids has been studied as a possible mechanism for increasing the transport rate through the geosphere.

Models describing radionuclide transport and including various aspects of filtration of colloids and stability as well as the interaction between radionuclides and colloids and the interaction between the colloids and the rock have been developed (e.g. *[Allard et al., 1991; Grindrod and Worth, 1990; de Cayeux et al., 1990: CEC, 1992])*. There does not yet appear to be a consensus on how a colloid transport model should be designed. One issue that has been discussed is whether the sorption of radionuclides onto colloids could be regarded as reversible or if it must be assumed that the radionuclides are irreversibly bound to the colloids. If the sorption is reversible, the influence of the colloids on the net transport of radionuclides will be negligible given the concentrations and sorption properties found for colloids in deep, saline and non-saline groundwaters *[Allard et al., 1991]*.

5.6.2 Transport capacity

The importance of natural colloids for the dispersion of radionuclides from spent fuel in a leaky copper canister has been assessed in SKB-91. A simple approach was taken. It was assumed that the radionuclides are irreversibly sorbed on the colloids and transported with the groundwater flow without retention *[Allard et al, 1991]*. Required for these calculations are, among other parameters, the concentration of colloids in the groundwater, S, and the sorption coefficients for the radionuclides on the colloids K_{part}. If it is assumed that the higher sorption coefficient values observed in the laboratory are the result of irreversible sorption then the concentration of radionuclides attached to the colloids C_s is given by

$$C_s = C \bullet S \bullet K_{part}$$

where C is the total concentration of the radionuclide in the water.

In SKB-91 a series of reference K_{part} values were selected for the radionuclides; for the actinides, lanthanides and technetium a value of 30 m^3/kg was used, for radium and lead 10 m^3/kg, for strontium and nickel 1 m^3/kg and for cesium 0.01 m^3/kg. This selection is based on laboratory experience of radionuclide sorption on colloids. In these experiments the colloids generated consist of silica, clay and other mineral phases that are anticipated in granitic rock.

Analyses of concentrations in groundwater of colloids have a tendency to overestimate the content. For example, fine particles of quartz and clay may remain from the drilling of the sampling well; furthermore, clay particles may be mobilised by pumping. Carbon dioxide (uptake or degassing) and oxygen may cause precipitation of colloids composed of calcite and ferric hydroxides respectively. Groundwater mixing during sampling can also cause precipitations of colloids such as iron sulphide, sulphur, ferric hydroxide, calcite etc. The considerations that are needed for sampling and analysis of colloids are described by *[McCarthy and Degueldre, 1993]*. Generation of colloids in groundwater and the role of colloids for contaminant transport are also discussed in the quoted report.

Deep Swedish granitic groundwaters have been analysed for their content of natural colloids using an in situ filtering system isolated from the influence of the atmosphere. The results were used in SKB-91 to select values of the colloid concentration S. A central value of $S=0.1$ mg/L and a maximum value of $S=0.4$ mg/L were selected. The colloid composition was also analysed in order to guide radionuclide sorption experiments on colloids and also to check the relevance of the samples.

The outcome of the colloid transport calculations for SKB-91 was that no significant radiation dose (calculated dose was below ICRP limits) was obtained even if irreversible sorption was assumed. However, the results depend both on the experimental results and the assumptions made. Colloid analysis is difficult. The composition can vary in nature and also the concentration of colloids is probably sensitive to groundwater chemistry in general. A dilute water tends to stabilise colloids. At low enough concentrations of cations even the bentonite clay used as backfill can release colloidal clay particles *[Le Bell, 1978]*. The concentration of a certain cation, needed to destabilise a colloid, is designated as the critical coagulation concentration, ccc. Divalent ions such as calcium are more efficient in preventing colloid formation than monovalent ions such as sodium.

Poços de Caldas

The two sites in Poços de Caldas; Morro do Ferro and the Osamu Utsumi mine, have been sampled for colloids. Morro do Ferro, a thorium/rare-earth mineralisation which is rich in thorium and lanthanides, was well suited to investigate the role of colloid transport *[Chapman et al, 1991]*. The high positive valencies of these elements (three- and tetravalent) give them a strong tendency to sorb onto particulate matter. In addition some uranium is present on the colloids. The intense lateritic weathering generates iron hydroxides and clay minerals which form colloids. The surface waters are rich in humic substances which can form organic colloids or help to stabilise inorganic colloids. The groundwater is very dilute. Potassium is the dominating cation coming from the weathering of potassium feldspar. Typical concentrations of potassium are in the range 0.1 to 10 mg/L and sodium is in the range 0.1 to 0.5 mg/L. The most abundant divalent cation is calcium with concentrations between 0.1 to 7 mg/L. This may be compared with typical concentrations in deep swedish groundwaters which are similar for potassium but orders of magnitude higher for sodium and calcium. The contents of the most important cation for coagulation of colloids, calcium, is 20 to 4000 mg/L in average Swedish groundwaters at repository depths.

The total concentration of colloids at depth in Morro do Ferro groundwaters is less than 1 mg/L which is roughly similar to what has been obtained in Sweden and elsewhere. The colloids in Morro do Ferro are associated with thorium, lanthanides and uranium. Of the total dissolved thorium 97 % is associated with the colloids and the corresponding figure for the lanthanides is in the range 80 to 90 %. Only a minor fraction of uranium is associated with colloids.

It is interesting to note that the uptake of three- and tetravalent elements are much higher than anticipated from laboratory measured sorption coefficients. This value, which was also used for calculation of colloid transport of three- and tetravalent actinides was 30 m^3/kg which implies that /only 3 % is bound to colloids. The much higher uptake on the colloids in Morro do Ferro may be explained by their high content of humic matter which gives them strong sorption properties.

The Osamu Utsumi uranium mine was also sampled for colloids *[Chapman et al, 1991]*. Again the weathering is intense, generating iron hydroxides and clay minerals which form colloids and particles. The waters are dilute but slightly higher in their contents of dissolved solids than Morro do Ferro. The potassium concentration is in the range 5 to 45 mg/L, sodium 0.1 to 2 mg/L, calcium 0.5 to 115 mg/L and magnesium 0.05 to 4 mg/L. The near-surface recharge water is acidic due to oxidation of pyrite. Deeper into the formation the pH increases to between 5.5 and 6.5, mainly due to reactions with potassium feldspar.

The redox fronts at the Osamu Utsumi mine, where uranium has precipitated as pitchblende close to the front on the reducing side, has been taken as an analogue for the scenario of a redox front caused by radiolysis from disposed spent fuel exposed to groundwater (see Section 4.3). It has been debated as to whether such a front can generate mobile uranium colloids or other radionuclide colloids. For example, if uranium and other redox sensitive radionuclides are leached from spent fuel and oxidised by radiolysis, they may subsequently become reduced and precipitated at the redox front. In principle colloidal particles can be generated in this way. However, even if this happens, it is not certain that the colloids are mobile. As a matter of fact, laboratory experiments show that pure actinide colloids tend to become fixed by sorption on the rock mineral surfaces *[Olofsson et al., 1983]*.

The colloid fraction from the Osamu Utsumi mine was isolated by filtering and the size range between 1.5 nm and 0.45 μm was defined as colloidal. The concentration of colloids is typically less than 0.5 mg/L which was surprising considering the intense weathering. The main components of the colloid fraction are ferric oxyhydroxides and organic matter. High resolution ESCA was used to show the presence of C-O and O=C-O groups which indicates humic substances. About 3 to 10 % of the dissolved organic carbon was present in the colloid fraction; the silicate mineral component of the colloids is very small.

Most of the uranium was found to be in true solution. Between 5 and 30 % of the uranium was in the colloid fraction and associated with colloidal iron and carbon. Using the sorption coefficient for uranium on colloids according to the SKB-91 safety assessment, 30 m^3/kg (reducing conditions), it would suggest that only 1.5 % was attached to the colloids. This difference may be explained by the high content of humic matter and ferrous hydroxides in the Osamu Utsumi colloids.

The concentration of uranium at depth is in general 3 to 15 μg/L, which was lower than expected considering the results from geochemical calculations of inorganic uranium solubility (0.2 to 10 mg/L). The solubility of uranium is evidently not influenced by colloids to any major extent. Also, there is no noticeable concentration of pure uranium colloids, as one would expect to find if precipitation of pure uranium colloids is an important mechanism at the redox transition.

Oman

The chemical environment of radionuclides in waste conditioned with cement and surrounded by concrete in a repository for low- and intermediate-level waste, would be highly alkaline and reducing. As colloids tend to be destabilised by high pH or high salinity; they are not likely to be of importance in cement pore water.

The hyperalkaline springs in Oman at the Arabian Gulf were studied as natural analogues to concrete repository conditions *[Bath et al., 1987]*. In one of the springs (Karku) colloids carrying uranium and thorium were suggested by filtering.

The water in the Karku spring had a sodium concentration of 258 mg/L, potassium 11.2 mg/L and calcium 72.0 mg/L. The pH was 11.4 (measured in situ), E_h= -363 mV and the temperature 35.7 °C. the concentration of iron was below the limit of detection ($<$0.01 mg/L) but the sulphide content of the water was reported to be as high as 26.0 mg/L (measured as the difference between total sulphur and sulphate concentration).

The Karku spring water sample had after filtration through a 0.45 μm filter showed a uranium concentration of 0.23 ± 0.01 ng/g. Filtering with a 0.1 μm filter removed the uranium to below the limit of detection. This could be explained by the existence of uranium-bearing colloids in the spring water, a conclusion further supported by the very high ^{228}Th/^{232}Th ratio of 178 ± 10 measured in the sample following the 0.1 μm filtration. The ^{228}Th isotope is produced by decay of ^{232}Th over ^{228}Ra. The α-recoil effect will thus help to liberate ^{228}Th to the solution and, if there are colloids present, they can sorb the thorium isotope and thereby stabilise it in solution. Organic colloids and colloids of clay were found on the filters which could have been components of the colloids. Calcite and iron oxide colloids were also found but they were probably created by precipitation during the filtering operation (CO_2 uptake and oxidation).

It was concluded that colloids capable of sorbing uranium and thorium had been indicated in one of samples of natural high pH water from Oman. Further investigations of the possibility to obtain colloids in cement pore water was recommended.

Maqarin

Hyperalkaline water has also been encountered elsewhere. The alkalinity of the Oman water resulted from contact with ultrabasic rock minerals, but this is not the only source. At Maqarin, in the northern part of Jordan, groundwater is found with a pH of around 12.5 due to natural occurrences of burnt lime. Preliminary attempts to sample colloids have been carried out, and indicated concentrations are below 1 mg/L, which is roughly what is generally found in deep groundwater anywhere. No significant colloid uptake of trace elements, which are abundant in Maqarin, have been indicated so far. Studies are continuing.

Alligator Rivers

Groundwater colloids were sampled at the Koongarra uranium deposit, Alligator Rivers area, using hollow fibre filtration *[Duerden, 1992a]*. The groundwater at the sampled depths (20 to 90 m) is dilute in character with a calcium content of 0.7 to 2.7 mg/L, magnesium 5 to 22 mg/L, sodium 1.0 to 2.2 mg/L and potassium 0.4 to 1.3 mg/L. The dominating anion is bicarbonate. The water is also relatively rich in iron (0.05 to 22 mg/L) and silica (5.3 to 15.7 mg/L). In situ pH measurements range from 6.1 to 7.0 and E_h values from +75 to +225 mV. The water is reported to be very low in TOC.

The colloids were sampled by hollow fibre filtering of the less than 1 μm fraction (prefiltering used). Isotope and chemical analyses demonstrated that ^{238}U, ^{230}Th, ^{227}Ac and iron were to some extent retained. For ^{238}U the retention in the filters was 1 to 3 %, for ^{230}Th 12 to 82 % and for iron 0.5 to 1.4 %. The retention of ^{227}Ac was high but the activity too low for accurate quantification. The concentration of uranium in Koongarra groundwater, where ^{238}U is the main isotope, is in the range 0.1 to 440 μg/L. The activity of ^{230}Th was considered very low ($<$0.05 dpm/L), particularly in comparison to its relative abundance in the surrounding rock. This was taken as an example of the very low solubility of thorium. It was pointed out that a fraction of the colloids might have been generated along with the sampling procedure.

SEM/EDAX analyses showed that individual colloids tended to be enriched in elements such as Ti, Ca, Mg, Si, Zn, Au, Al, S or Ni. However, iron was indicated as the major element in the colloidal particles. Considering the variation in iron concentration in groundwater, and the measured separation of iron by ultrafiltration. the concentration of colloids should be less than 0.5 mg/L provided that they are mainly composed of oxidised iron.

It was concluded that the only elements significantly enriched in the colloid fraction are iron. thorium, actinium and uranium. It was suggested that a mobile ferrihydrite colloid is present in the groundwater onto which radionuclides are sorbed.

Broubster

At this site, shallow groundwater is transporting uranium and associated elements from lime-rich sediments over a distance of roughly 100 m to a peat bog, which is being enriched in uranium *[Read, 1988]*. The water has a calcium concentration of 3 to 44 mg/L, sodium 15 to 22 mg/L and magnesium 1 to 6 mg/L. The dominating anion is bicarbonate followed by chloride and sulphate. Organic matter is abundant in the water and the TOC ranges from 12 to 142 mg/L. The waters are oxidising with E_h ranging from +201 to +419 mV and the pH is slightly on the acidic side (5.3 to 6.7). The iron concentration ranges from 0.04 to 3 mg/L. Uranium concentrations are between 3 and 21 μg/L.

The investigation at Broubster *[Longworth et al., 1989]* indicate that thorium is strongly associated with particulate matter in the groundwater. Part of the thorium is associated with organic matter in the groundwater and the rest mainly with iron oxyhydroxides. The mobility of thorium, however, appeared to be very low which may be explained by filtration in the soil at the site. An alternative explanation is that thorium is reversibly bound to the particles.

The association of uranium with organic particles has been mentioned by some investigators.. In a more recent publication *[Read et al., 1991]* the importance of fulvic acids was pointed out. It would appear that the dissolution and transport of uranium at Broubster is facilitated by the formation of complexes with fulvic acids. Whether particulate organic matter is contributing is less certain at present.

Krunkelbach

Groundwater and minerals from the Krunkelbach uranium mine in Menzenschwand, southern Germany, have been sampled and analysed *[Hofmann, 1989]*. The host rock is granitic, and most of the groundwater inflow occurs at the 240 m level. The content of stable isotopes in the groundwater (oxygen-18 and deuterium) and the content of N_2 and Ar were used to calculate the temperature and altitude of the infiltration area. The indicated recharge area is a high plateau on Feldberg 3 to 5 km north of the mine.

The chemical composition of the groundwater in the mine is normal and characteristic for rapid infiltration in granitic rock. the water is dilute and all samples had a very high oxygen content of between 8.2 and 9.4 mg/L. Mixing with surface water is indicated by the content of tritium which varies between 7.1 and 25.5 TU on the 240 m level. The surface water had an average tritium content of 25.7 ± 1.7 TU. There is the possibility that some of the tritium is generated in the uranium ore by spontaneous neutrons and the presence of high lithium contents (cookeite).

The sulphate in the water results from oxidation of pyrite associated with the ore. Uranium is being slowly dissolved from the ore by the oxidising water and phosphate is being precipitated. During the oxidation of the deposit uranium (ranging from 0.6 to 3.3 percent by weight) has been fixed by iron oxyhydroxides which are partly crystallised to goethite. Enrichment of radium in secondary baryte was also indicated. The low mobility of lead during oxidation was demonstrated.

The groundwater contained between 0.006 and 5.9 mg/L of suspended material $>0.22\ \mu m$. The existence of colloids was also indicated by the large variations in the concentrations of aluminium, iron and manganese between different samples. The suspended material was composed of clay minerals, quartz, gorceixite and amorphous iron oxyhydroxides. The suspended clay fraction was higher in magnesium (about three limes) and titanium (one to two orders of magnitude) than the clay in the deposit. Interestingly, it was concluded that these clay colloids were carried by the flowing groundwater from a gneiss formation rich in magnesium and titanium, situated at a distance of 1 to 2 km. If this conclusion is correct, it implies that colloids in the form of clay colloids can be transported over distances of 1 - 2 km by groundwater flow in fractured granitic rock.

Natural uptake on uranium and thorium on suspended matter in the Krunkelbach mine was analysed by *[Jeremy et al, 1989]* who concluded that uranium and thorium are transported by colloidal iron oxyhydroxides. Up to 10 % of uranium and all of the thorium was reported to be associated with the iron(III) colloids.

5.6.3 Reversibility of sorption on colloids

The influence of reversibility of radionuclide sorption on the colloids and the importance of that for contaminant transport is outlined in the report *[Allard et al., 1991]*. It is assumed that the radionuclide can sorb reversibly by linear sorption on the rock measured by the sorption coefficient K_d. It is further assumed that the radionuclide can sorb on the colloidal matter with a sorption coefficient K_{part}. The radionuclide will become distributed between the three phases: groundwater, rock and colloids. The amount of radionuclide sorbed to the rock will be decreased by the competition with the colloids. This can be expressed by using a sorption coefficient K_{eff} which is the ratio of the concentration of radionuclide on the rock, $K_d \bullet C$ to the total concentration of radionuclide in the water, $C + C \bullet S \bullet K_{part}$.

$$K_{eff} = K_d/(1 + S \bullet K_{part})$$

Consequently the uptake of radionuclides on the rock is decreased a factor $1/(1 + S \bullet K_{part})$ compared to sorption in the absence of colloids. It can be demonstrated *[Allard et al, 1991]* that the retardation of radionuclides migrating with the flow of groundwater will be reduced by the same factor. If we have a colloid concentration of $S=1$ mg/L and the sorption on the colloids are as high as 30 m^3/kg the K_d is still only decreased by 3 %. This is unimportant compared to the uncertainty in the K_d value and the effect of colloids on the retardation will consequently be totally negligible. Therefore, the question of whether uptake on colloids is reversible or not is important for the function of the rock as a barrier to radionuclide dispersal.

The interaction between particulate matter and dissolved species in the groundwater have been studied in several natural analogue projects by investigation of the isotopic equilibria/disequilibria in the natural decay chains, notably $^{234}U/^{238}U$ and $^{230}Th/^{234}U$, and the relative concentrations of, for example, rare-earth elements. These entities are measured on the host rock, on water samples and on the colloids. Some of the observations are summarised below.

Isotopic equilibrium methods

The activity ratios $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ have been measured at e.g. Alligator Rivers, Morro do Ferro, Osamu Utsumi, Cigar Lake and Broubster. For material that is old enough for radioactive equilibrium to develop (i.e. a couple of million years for $^{234}U/^{238}U$) these activity ratios should be close to unity. Several physical and chemical processes can offset the ratios from their equilibrium values. For instance α-recoil will increase the ratio $^{234}U/^{238}U$ in the groundwater above unity. The activity ratios in the groundwater can be compared with those obtained for the colloids and the host rock. If the ratio $^{234}U/^{238}U$ is similar in the water and in the solid phase this could be an indication of a dynamic equilibrium process. Below, some activity ratio determinations are examined with respect to their potential implications for the interaction between radionuclides and colloids in the groundwater.

In the Alligator Rivers Natural Analogue Project several studies of colloids have been conducted. The ratio $^{234}U/^{238}U$ has been found to vary between 0.74 and 1.12 *[Ivanovich et al., 1988a]*. The values for colloids and the groundwater are similar indicating a potential dynamic equilibrium. Particles filtrated out of groundwater samples from Alligator Rivers were extracted with acid *[Payne, 1991]*. The extractable part of the particles contained an excess of iron, manganese and aluminium compared to solutions obtained from extraction of bore cores. This was interpreted to indicate that the extractable phases consist of amorphous phases. The activity ratio $^{234}U/^{238}U$ in the extract was below unity and close to the ratio measured in solutions that had passed ultrafiltration. It was concluded that the extractable (amorphous) phases were accessible to water whereas the residual phases, which had higher $^{234}U/^{238}U$ ratios, contained inaccessible uranium.

The measured activity ratios $^{234}U/^{238}U$ have been found to be similar on colloids and in groundwater both at Morro do Ferro and Osamu Utsumi *[Chapman et al., 1991]*. At Morro do Ferro this ratio varies in the range 1.5-2.1 and at Osamu utsumi between 1.0 and 2.6. The ratio in the host rock at Morro do Ferro has been found to be 0.9-1.2, i.e. considerably lower than in the groundwater and on the suspended matter. A possible explanation to these data is that there is an equilibrium situation between dissolved uranium in the groundwater and uranium sorbed onto colloids. The higher ratios in the groundwater also indicate that ^{234}U is dissolved preferentially compared to ^{238}U, possibly due to α-recoil.

The ratio $^{230}Th/^{234}U$ is significantly higher on the colloids (0.1-0.9) than in the groundwater (0.002-0.09) indicating that thorium is more strongly sorbed onto the colloids than is uranium. This is an expected outcome considering the chemical properties of thorium and uranium.

The investigations at Broubster *[Longworth et al., 1989]* also indicate that thorium is strongly associated with particulate matter in the groundwater. Despite this, the mobility of thorium is low. There are at least two possible explanations to this; the thorium is either reversibly bound to the colloids or the colloids could be retarded by filtration in the porous medium on the site. While thorium appears to be bound mainly to inorganic colloids such as amorphous iron oxyhydroxides, the uranium seems predominantly attached to organic colloids.

In a more recent publication *[Read et al., 1991]* the uranium is said to be bound to carboxyl functional groups in the peat. The mobilisation of uranium before entering the peat is facilitated by dissolution of intergranular cement in the host sandstone and by the presence of fulvic acids to complexate the dissolved hexavalent uranium. The prerequisites for the development of the Broubster uranium anomaly are said to be a uranium-rich source, availability of oxidising groundwater, complexing ligands (fulvic acids) to keep the uranium in solution during transport from the source to the peat deposit and a peat deposit to fix the uranium.

The activity ratio, $^{234}U/^{238}U$, in the ore at Cigar Lake *[Vilks et al., 1991]* varies between 0.8 and 1.0. The activity ratio in water samples and on particulate matter suspended in the groundwater is substantially higher and similar, on average 1.99 on particulate matter and 1.93 in water samples. It should be noted that these are mean values of a number of measurements that vary widely.

The higher ratios in water and on colloids compared to the ore are interpreted as a result of preferential dissolution of ^{234}U from the ore, possibly due to α-recoil, and reversible sorption onto the colloids. In-situ distribution coefficients were calculated for the equilibrium between dissolved uranium and uranium on colloids. As these distribution coefficients were found to vary significantly, it was concluded that the uranium may not be in sorption equilibrium.

Relative concentrations of rare earth elements

At Morro do Ferro *[Chapman et al., 1991]* one of the main objectives was to study the extent of transport of thorium and rare-earth elements. Concentrations of thorium and rare-earth elements were measured on rock samples, in groundwater and on colloids suspended in the groundwater. The samples were taken at two positions. The first position (MFl0) was located in the weathered and unsaturated zone close to the mineralisation. The second position (MF12) was located downstream from the first position and in the saturated part of the rock.

The contents of thorium and rare-earth elements on the suspended colloids were high (1 000-4 000 μg/g) at the first position whereas it was considerably lower (20-300 μg/g) at the second position. This suggests that there is little colloidal transport of these elements between these two points.

This is further supported by the rare-earth element patterns from colloids and groundwater. Figure 5.5 shows the chondrite-normalised rare-earth element concentrations obtained at the two sampling points. At MF10, i.e. in the weathered and oxidised zone, a negative cerium anomaly occurs. It has been speculated that this could be due to the very low solubility of the tetravalent cerium hydroxide, $Ce(OH)_4$, compared to trivalent rare-earth elements. This anomaly is not present at MF12 where the pattern resembles the pattern obtained for rock samples. The fact that the cerium anomaly is not observed downgradient indicates either a lack of transport of suspended particles (if sorption of rare-earth elements is either irreversible or slow) or rapid dynamic equilibrium between trace elements in the groundwater and those sorbed onto the colloids. The prospect of either total removal of colloidal particles by for example filtration or reversibility in the uptake of radionuclides on colloids would in both cases render colloid transport insignificant in performance assessment *[Allard et al., 1991]*.

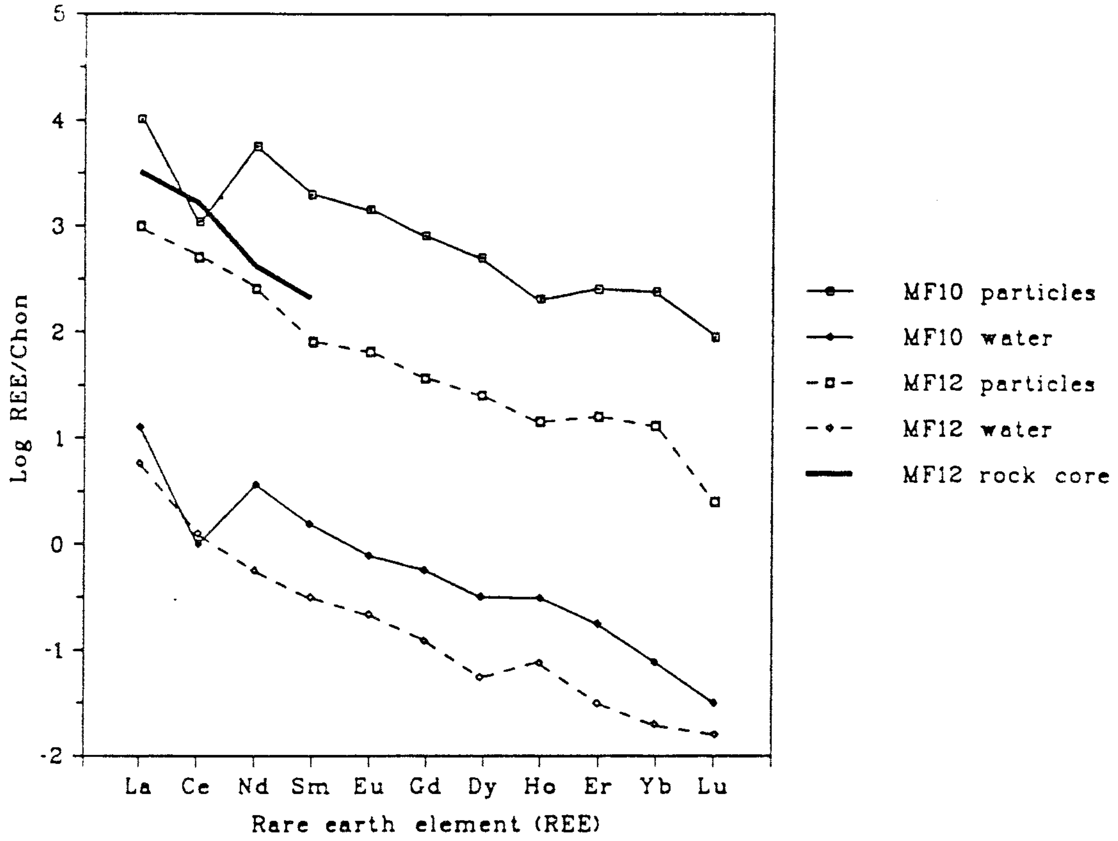

Figure 5.5 Chondrite-normalised rare-earth element patterns in typical rocks, groundwaters and corresponding suspended particles from Morro do Ferro (from *[Chapman et al., 1991]*)

5.6.4 Conclusions

Important issues concerning the influence of colloids on the safety of radioactive waste disposal are: concentration and composition of colloids in natural deep groundwater, uptake - reversible or irreversible - of radionuclides on colloids, mobility of colloids and the generation of colloidal particles in the near field of a repository.

It is difficult to sample and analyse colloids. There is a tendency to generate particles by the sampling procedure and concentrations reported are generally overestimates. Colloid analysis have been made in the course of many analogue investigations. The concentrations are roughly around 1 mg/L and they are composed of iron oxyhydroxides, clay particles (illite, kaolinite and smectite), quartz, calcite and sulphur containing species. Humic substances also appear as colloids or as coatings on inorganic particles.

Uptake of uranium and three- and tetravalent element ions (thorium and REE) on colloids have been analysed in groundwater coming from different mineral deposits. The uptake of three- and tetravalent cations on the particles were higher than expected from sorption experiments where samples of the minerals were used instead of colloids.

Concentration of colloids and sorption coefficients for radionuclides on colloids have been used to model colloid transport from a defect canister containing spent fuel in a repository hosted by granitic rock. The analogue observations generally support the input data used. Moreover, the two assumptions of irreversible sorption on the colloids and unretarded transport appear as overconservative when compared to the observations made in the Poços de Caldas analogue study. These results are either explained by reversible uptake or that the colloids are not mobile. Other analogues generally support this view. However, one notable exception of high colloid mobility has been reported from the study of the Krunkelbach mine. Clay particles were found in the groundwaters from the mine. A gneiss formation at a distance of 1-2 km was suggested as the source of the clay. More studies of colloid transport in hard crystalline fractured rock may therefore be warranted in order to confirm observations of reversibility and immobility as indicated at Poços de Caldas.

A particular question in connection with the leaching of spent fuel in a repository is whether, for example, uranium colloids can be generated by precipitation. These colloids can be anticipated when uranium is migrating from a radiolytically oxidised near field to the normal reducing deep rock groundwater environment. However, no such evidence of particle generation has been found at the redox fronts at Poços de Caldas or elsewhere.

6. The role of microbes for repository performance

6.1 General

In Sweden, bacteria have been found in groundwater samples taken from depths down to 1 km in granitic rock. The sampling was performed downhole between packers using a special device employing sterilised bottles to collect groundwater flowing from fractures in the rock. Opening and closing of the bottles was remotely controlled. Methane bacteria and sulphate reducers were identified *[Pedersen, 1989 and 1991]*; the ability of bacteria from deep groundwater to fix carbon dioxide has also been demonstrated *[Pedersen et al., 1991]*. Furthermore, it has been shown that microorganisms at depth occur both suspended in the groundwater and sorbed onto the mineral surfaces of hydraulic rock fractures *[Pedersen et al., 1991; Pedersen and Albinsson 1991]*.

Microorganisms play an important role in the evolution of the groundwater chemistry *[Stumm and Morgan, 1981]*. The biological life in the root zone reduces the oxygen content and introduces carbon dioxide into the infiltrating groundwater. The carbon dioxide reacts further forming carbonates: sodium and calcium bicarbonate and carbonate. In addition to the carbonate acting as a pH buffer in the groundwater, the carbonate ion is an important complex forming anion which can influence the solubility of certain trace metals, e.g. uranium.

Other important biological processes influencing groundwater composition are iron oxidation and sulphate reduction. The microbiological reduction of sulphate to sulphide is well documented *[Stumm and Morgan, 1981]*. It has also been indicated by the investigations of deep groundwater in Stripa and is being further studied in the Äspö Hard Rock Laboratory. An important recently described observation is the effect of iron(III)-reducing bacteria. These bacteria will use organic substrate and hydrogen like the sulphate reducers and thereby compete with them. There is evidence from studies of natural systems that iron(III)-reducers influence the groundwater composition *[Chapelle and Loveley, 1992]*.

Bacteria are, of course, limited by the laws of thermodynamics and by the supply of nutrients. On the other hand they are able to mediate geochemical reactions which would otherwise not have occurred because they are kinetically hindered. A good example of this is sulphate reduction, which will not happen in nature at ambient temperatures without help from bacteria.

Lack of nutrients or hostile environments characterised by high pH, high temperatures, radiation etc, can kill or inactivate the microbes. There is no guarantee, however, that sterility is achieved by such influences in and around a nuclear waste repository *[Tittel et al., 1991]*. Many strains of bacteria are known to survive long periods of starvation and other forms of environmental stress.

The possible effects of bacteria have been discussed in the performance safety assessment of both high- and low-level waste disposal. A number of processes of importance for long time safety can be influenced by bacteria such as: gas generation, corrosion, redox reactions, formation of complexing agents and transport of radionuclides with groundwater. To take the pessimistic view, for example, that any reaction that can be caused by microbes will occur in a repository and that the only limiting factor would be the availability of nutrients, is an overconservative assumption. In order to reach realistic or reasonably conservative estimates of the influence from bacterial processes, geochemical research, laboratory investigations and studies of natural analogues are performed. A series of examples will be given below on the use of analogue observations for the assessment of bacterial influence on waste disposal safety.

6.2 Gas generation

Production of gas in a repository for low- and intermediate- level radioactive waste is an important issue. It is necessary that the repository design allows for gas to escape without damaging the structure. The generation of a separate gas phase can also displace contaminated water from the repository, pressing it out into the surrounding groundwater. Another effect is the influence on hydraulic flow if gas escapes into the rock.

The prime source of gas identified in the performance assessment of a low- and intermediate-level waste repository is the anaerobic corrosion of steel components, eg reinforcement in the concrete. However, gas generated by microbes has also been anticipated. Microorganisms can produce gas directly by the decomposition of organic materials, such as cellulose, or indirectly by enhancing the corrosion rate of steel.

Production of methane and carbon dioxide in the cellulosic waste of the Swedish SFR repository was estimated by comparison with peat bogs and river bottom sediments generated by the release of cellulose fibres from pulp and paper mills. Here the conditions are anaerobic, the temperatures are comparable, and the gas is generated by the activity of methane generating bacteria. The outcome of this analogy was that less than 1 m^3 NTP per metric tonne of cellulosic waste per year was to be expected *[Rennerfelt and Meijer, 1986]*.

Indirect gas generation resulting from a bacterial increase of corrosion rate was also assessed for SFR. Biodegradation of bitumen could in principle generate carbon dioxide which in turn enhances steel corrosion. Normally the carbon dioxide in a repository is consumed by reactions with concrete, but in this case corrosion on the inside of steel drums containing a bitumen matrix was anticipated. However, within the drums it is also possible that bacteria will generate carbon dioxide and lower the pH without the buffering effect of concrete. Laboratory studies of bitumen degradation by bacteria was the main source of information to this process. However, similar degradation processes have also been observed in rock caverns in Sweden where crude oil is being stored on a layer of groundwater. Some of the bacteria cultures used in the laboratory experiments had been taken from these oil storage sediments *[Hjalmarsson and Roffey, 1985]*. According to the experiments some slow degradation of bitumen could not be excluded. However, it was possible to treat corrosion collectively for the entire iron content in SFR using a conservative estimate of iron corrosion rate.

It is also interesting to note that bitumen occurs naturally and can be very old. Bitumen is present in notable quantities in the reactor zones at Oklo and has evidently survived the period of criticality. At Maqarin (Jordan) bitumen naturally occurs frequently in the rock (marl). Spontaneous ignition followed by incineration of the organic component of the marl has locally created "concrete conditions" by producing lime. Regardless of widely varying pH conditions, and regardless of the fact that sulphate is abundant in the groundwater as electron acceptor for sulphate-reducing bacteria, there are no apparent signs of bitumen degradation by microbes at Maqarin. However, neither the Oklo nor the Maqarin analogues have yet been fully interpreted in this context.

Gas generation (mainly hydrogen) in a repository for high level waste has also been considered *[SKB, 1983]*. As hydrogen diffusion through a bentonite backfill is slow, a high enough production rate of hydrogen at a waste canister could therefore cause a separate gas phase to be created in the near-vicinity. Corrosion would be the most significant source of hydrogen if steel canisters are going to be used. Bacteria can, in principle, enhance the anaerobic corrosion of steel and thereby increase the production rate of hydrogen. Steel corrosion is treated below.

6.3 Corrosion

The effect of bacteria produced carbon dioxide on steel corrosion rates has been discussed in connection with the performance assessment of SFR, where the main focus was on hydrogen gas production as a result of corrosion *[Moreno and Neretnieks, 1988]*. However, bacteria driven corrosion of steel (both aerobic and anaerobic corrosion) has also been evaluated for high-level waste encapsulated in steel canisters according to the Swiss concept. Aerobic corrosion is expected to dominate until air trapped in the repository subsequent to sealing has been consumed; following this a long period of anaerobic corrosion will dominate. Reference was made to the widespread observation of steel casing failure in oil wells *[McKinley et al., 1985]*. Sulphate-reducing bacteria have been identified as the main cause of this effect. However, bacteria-induced corrosion was not regarded as critical in the Swiss study where the availability of nutrients and energy for the bacteria were expected to be limiting factor.

Sulphate-reducing bacteria have also been considered in the evaluation of the scenario for copper canister corrosion analysed in the Swedish KBS-3 concept. Lightning conductor plates which had been buried in the ground for 50 - 80 years were studied as analogues to determine the general corrosion and pitting factors of copper *[Mattsson, 1983]*. One of the three plates which was buried beneath the groundwater table exhibited sulphide corrosion generated by sulphide-reducing bacteria. This plate was less affected than the others and did not show any signs of pitting.

An important limiting factor to consider in the assessment of sulphide production by sulphate reducing bacteria is the supply of electron donors. Organic material, methane and hydrogen have been reported as candidates *[Stenhouse and Grogan, 1991]*. A potential source of organic material noted in the KBS-3 concept is the bentonite buffer. In deep groundwater, methane is present in low concentrations and hydrogen, also found in small amounts, can also be generated by, eg corrosion.

Another important factor to consider is whether the reaction can be localized or not. An interesting analogue in this context is the occurrence of reduction spheres in haematitic rocks *[Hofmann, 1990]*. The reduction spheres have diameters from mm to dm, and constitute reduced areas in an otherwise oxidised rock. Sulphide ore minerals are sometimes found inside the spheres. The processes that created these textures may not yet be completely understood, but the action of sulphate-reducing bacteria has been suggested to explain the main features of the reduction spheres.The action of iron(III)-reducing bacteria described by *[Chapelle and Loveley, 1992]* could perhaps also explain the reduction process. Even better would be a combination of sulphate reduction and iron(III)-reduction. Another observation is that the extent of reduction is such that an external source of reductants must be assumed. The amount of organic material originally contained in the reduction sphere would probably have been inadequate.

A further evaluation of this analogue with the aim to elucidate the possible consequences of sulphate reduction seems worthwhile. Disturbing factors include the localised nature of the phenomenon, the production of sulphides and the use of some unknown external source of reductants. The positive features that deserve to be mentioned are the reduction of iron(III), the trapping of trace metals inside the spheres, eg uranium, and the long time a reduction sphere needs to develop.

Analogues have also been used to obtain information on the oxic corrosion of copper. Oxygen trapped in the repository after sealing can result in the corrosion of the canisters. Even if limited, oxygen needs to be considered because it can cause pitting. Two of the lightning conductor plates previously mentioned had been subject to oxic corrosion and the pitting factor determined *[Mattsson, 1983]*.

Microbiologically induced oxic pitting corrosion has been observed in copper pipes for municipal waters *[Bremer and Geesey, 1991]*. The bacteria causing the trouble have in some cases been isolated and further tested in laboratory experiments with copper corrosion. The formation of a biofilm on the copper surface was found to be an important factor for the corrosion process.

6.4 Redox reactions

Sulphate reduction by bacteria using organic matter, methane or hydrogen as electron donors have been discussed above. This reaction can in principle have negative consequences for the performance of canisters, but it will also lower the solubility of some radionuclide elements by decreasing the redox potential and generating iron(II) and/or sulphide. In the absence of bacteria, sulphate reduction would not occur at ambient temperatures.

Other reactions such as oxidation of iron(II), oxidation of sulphide minerals and reduction of uranium(VI), are also important and may be catalysed by bacteria. In these cases it is important to prove that the reactions are reliable, and preferably they should occur in the absence of microbes. A good example of this is the oxidation of bentonite, which contains divalent iron and pyrite. After the sealing of the repository and bentonite saturation with water, the iron(II) and the pyrite can react with the trapped oxygen. These reactions will transform the system into a reduced state and thereby stop any further oxidation corrosion of the canisters by trapped air.

A similar situation occurs during the reduction of oxidants released by radiolysis of groundwater caused by exposed waste. Both the bentonite and the surrounding rock can act as a redox buffer. Most probably these reactions are reliable in the sense that they do not necessarily require microbial activity.

One conclusions from the observations of the redox front in the Osamu Utsumi uranium mine in Poços de Caldas is that the oxidation of pyrite is relatively fast, when compared to diffusion, and reliable. Microbes were sampled at the front and, astonishingly enough, sulphur-oxidising bacteria were not found *[Chapman et al., 1991]*. This is not proof but rather a strong indication that pyrite oxidation at a redox front will also proceed as a series of pure inorganic reactions under these circumstances.

Reduction of dissolved hexavalent uranium at a redox front is another interesting reaction from the performance assessment point of view. It can be expected to show a certain sluggishness, and indeed uranium(IV) is not precipitated immediately but a few centimetres ahead of the redox front on the reducing side. Uranium is precipitated as pitchblende nodules, often together with secondary pyrite. The role of microbes in these reactions was investigated in the Poços de Caldas project but no clear answer was obtained.

6.5 Formation of complexing agents

Bacteria can generate organic acids that form strong complexes with many metal ions. Carboxylic acids generated as byproducts from bacterial decomposition of organic waste are not very strong complex formers. More serious effects can be expected, eg from substances deliberately released from some bacteria in order to complex iron *[Brainard et al., 1991]*.

The influence of organic complexing agents from bacterial action or other reactions, eg hydrolysis by concrete porewater, are generally accepted as possible consequences. Therefore, organic complexing agents are assumed in the performance assessment of low- and intermediate-level waste disposal *[Rosevear, 1991; Wilkins, 1987]*. Solubility limits and sorption coefficients are lowered accordingly.

For the assessment of high-level waste disposal safety, generally no influence of organic substances on the solubility is accounted for. The sorption coefficients are sometimes lowered in order to account for the influence of humic and fulvic acids. However, these substances are not expected to contribute to the solubility to any significant extent *[SKB, 1983]*. Therefore, the production of strong complexing agents by bacteria would become a problem for the near-field as a barrier to radionuclide dispersal by increasing the solubility of many important radionuclides, and probably also increasing their mobility by diffusion in the backfill etc.

Analogue observations are important as a means of ruling out this possibility. It is possible to measure trace element concentrations in groundwater and to identify their corresponding mineral phases, which have to be abundant enough to saturate the water. The geochemical environment, and in particular the groundwater chemistry, will have to be well characterised beforehand. These trace elements are in some instances similar to those existing as radionuclides in waste, eg strontium, or they are chemical analogues to such elements, eg europium as an analogue to americium. By calculating the concentrations of these elements, assuming only inorganic speciation, and comparing the result to the measured concentrations, it is possible to see if any unexpected increase of solubility has occurred.

For this purpose it is an advantage to have observations from a wide variety of different geochemical environments and from environments similar to the repository. Such investigations have been carried out in high pH groundwaters in Oman *[Bath et al., 1987]* and Maqarin *[Tweed et al., 1991]*, in low pH groundwater under different redox conditions in Poços de Caldas *[Chapman et al., 1991]*, in the near-surface, slightly oxidising groundwater with a high content of organics at Broubster *[Read and Hooker, 1989]* as well as in deep, reducing and carbonate-rich groundwater from the clay horizons surrounding the Cigar Lake deposit (Work in progress). Similar studies are being planned from the crystalline bedrock environment at Palmottu. With a few notable exceptions the calculated solubilities are not exceeded. Higher than expected solubilities have generally been caused by errors in the thermodynamic constants used in the calculations or an erroneous assumption of which mineral controls the solubility *[Chapman et al., 1991]*. No significant influence of organic complex-forming substances on the solubilities have been found in the deep groundwaters at the above mentioned analogue sites.

6.6 Transport of radionuclides

The generation of complex-forming species and their possible influence on radionuclide migration has been discussed above. However, bacteria can also influence migration by taking up radioactive elements which have been dissolved in the water *[Pedersen and Albinsson, 1990]*. If the bacteria are attached to the surface of a rock fracture this will tend to cause retention of radionuclide transport. If, on the other hand, the microbe is suspended in the water phase, it can act as vehicle for the radionuclide, which will then become transported as a colloid.

In order to estimate the magnitude of this effect and the consequences to performance assessment, the following steps are taken: a) concentration of bacteria in deep groundwater is analysed, b) microbes are identified, c) uptake of sorbing radionuclides on relevant bacteria is measured in laboratory experiments. These data are combined and bacteria transport is treated as a form of colloid migration. This exercise has been carried out for SKB-91 which demonstrated that microbes do not have the capacity to influence radionuclide migration in any significant way *[Allard et al., 1991]*. However, the matter of bacterial transport is complicated. Some effects such as movement relative to the water phase and excessive uptake of trace substances are in principle possible if certain strains of bacteria are involved. Therefore, it is worthwhile to watch out for possible influence of bacteria in studies of radionuclide dispersion analogues in general, and colloid transport analogues in particular.

In the Poços de Caldas and Broubster studies colloid transport was investigated. Uptake of trace elements, eg Th, on colloidal particles was evident, but no colloid transport of any significance occurred. At these locations bacteria certainly had opportunities to develop. At Morro do Ferro the near-surface groundwaters are rich in organic matter, and in the Osamu Utsumi uranium mine there is an active redox front through which recharge water has to pass in order to evolve to constitute deep groundwater. If there is no significant colloid transport noted, then the influence of bacteria on migration must also be negligible.

6.7 Present status and recommendations

In connection with the performance assessment of radioactive waste disposal, the potential effects of microbial activities have been addressed on issues such as:

- gas generation
- corrosion
- redox reactions
- formation of complexing agents
- radionuclide migration

Gas generation by anaerobic bacterial decomposition of organic material is of importance for underground disposal of low and intermediate level waste. Studies of analogues and natural systems in general are important, and are being carried out in different countries.

Bacteria can influence the corrosion of copper and steel by generating sulphide (copper and steel) and carbon dioxide (steel). The prerequisites for these reactions and the potential effect on high level-waste canisters have been discussed. Such bacterial processes have been sought for in connection with material analogue investigations. Considering the importance of this issue, the scope has been enlarged such that sulphate reducing bacteria, their substrates and products are being looked for in many natural systems. This also includes analogue studies where microbial investigations can be integrated with the rest of the geochemical studies.

Bacteria mediated redox reactions are in general favourable for the safety of underground radioactive waste disposal. Examples of such reactions are oxygen consumption and uranyl reduction. However, even though we would like to see these reactions occur without the influence of microbes, it is necessary to include potential bacterial activity when interpreting observations of redox reactions in natural analogues, other natural systems and even in laboratory experiments, so that any influence they may have can be accounted for.

Carbonate ions, humic and fulvic acids are presumably the most important complex forming species in groundwater. Their presence can be traced to biological activities in the overlying soil root zone. However, it is important to know if strong complex forming agents are generated by, for instance, degradation of organic material in the waste itself or in other parts of the repository. Such studies have been performed for low and intermediate level waste. In fact, there are indications that bacteria would rather be an advantage by destroying certain difficult organic substances in the repository. The bacterial products were on the other hand fairly harmless. Also, no increase in solubility have ever been found at any analogue site. The dissolved trace elements which were related to waste nuclides were all accounted for by the normal groundwater composition. However, the matter of complex formation is important to safety assessment. An increase in concentration due to a strong complexing agent can in principle increase the release by the same factor (at least for long lived radionuclides).

Therefore, such microbial effects should be searched for in different environments. It can be made part of most analogue studies.

Microbes can influence radionuclide transport by taking up radionuclides from solution or by covering mineral surfaces. However, the normal concentration of bacteria in deep groundwater is too low to be of any importance for transport of radionuclides. Bacterial cover on mineral surfaces is possible, but this will hardly influence the retention. Also no specific bacteria carried trace metal transport have been noted that can be distinguished from other colloid transport at the analogue sites. However, the field is new, so it is recommended that bacteria concentrations are measured in different deep groundwater systems and that they are also characterised. It is of particular interest to perform such analyses at natural analogue sites where waste relevant elements are abundant and where colloids are simultaneously being sampled and analysed.

Search for microbes, signs of their influence and analysis of bacteria generated products should be part of any mayor analogue study, considering the potential influence on performance assessment. Specific microbe oriented analogue investigations should be considered in certain areas such as degradation of organic materials and redox reactions. Important bacterial mediated redox reactions are for example anaerobic reactions with organic compounds and hydrogen as electron donors and sulphate, iron(III) or uranyl as electron acceptors.

7. The Effect of Glaciation on Repository Performance.

7.1 Introduction

The onset of a future glacial conditions, coinciding with the projected life-span of a permanent repository for high-level radioactive waste, is cause for some concern regarding the long-term assessment of repository safety performance. It is quite clear that cyclic glaciations have occurred within recent geological time, and will very probably continue to occur, at least within the initial important 100 000 years, and most likely throughout the estimated time of high-level spent fuel containment, i.e. one million years (Ma). It is therefore important to put the life-span of the repository into a glacial perspective.

Predicting the performance of a repository during a major glaciation cycle is beset with substantial uncertainty. The possibility of the repository bedrock surviving impact from the harsh conditions imposed by an extensive glaciation, as well as the risk that related changes in groundwater hydraulics and chemistry, could threaten the integrity of the multibarrier system. Furthermore, what will the impact by man be when he intermittently returns during the more hospitable "warm periods"?

This short account on the potential influence of glaciation on repository performance is based mainly on a comprehensive overview of the world's ice ages and environmental changes by *[Eronen and Olander, 1990]* and references cited therein, and the description of an ice-age scenario that may influence repository performance, as envisaged by SKB and TVO, detailed by *[Ahlbom et al., 1991]*.

7.2 Timescales and Future Glaciations

Continental drift is believed to have played a major role in these long-term climatic changes. The oldest glaciation occurred around 2.3 billion years ago, followed by a series of large glaciations at 950-650, 450-430 and 310-270 Ma; the present Quaternary ice age actually began 17 Ma ago with the growth of large ice masses over Antarctica. Research into the Quaternary glaciations was first established in the Alpine region where four major glaciations were recognised. Subsequently, this model was widely adopted resulting in three major glacial epochs being recognised in Northern Europe and four in North America. These concepts, however, where radically changed with the application of the astronomical theory of climatic variation and the discovery that oxygen isotope measurements of oceanic sediments (and later glaciers themselves) provided an important key to climatic changes during the Quaternary period.

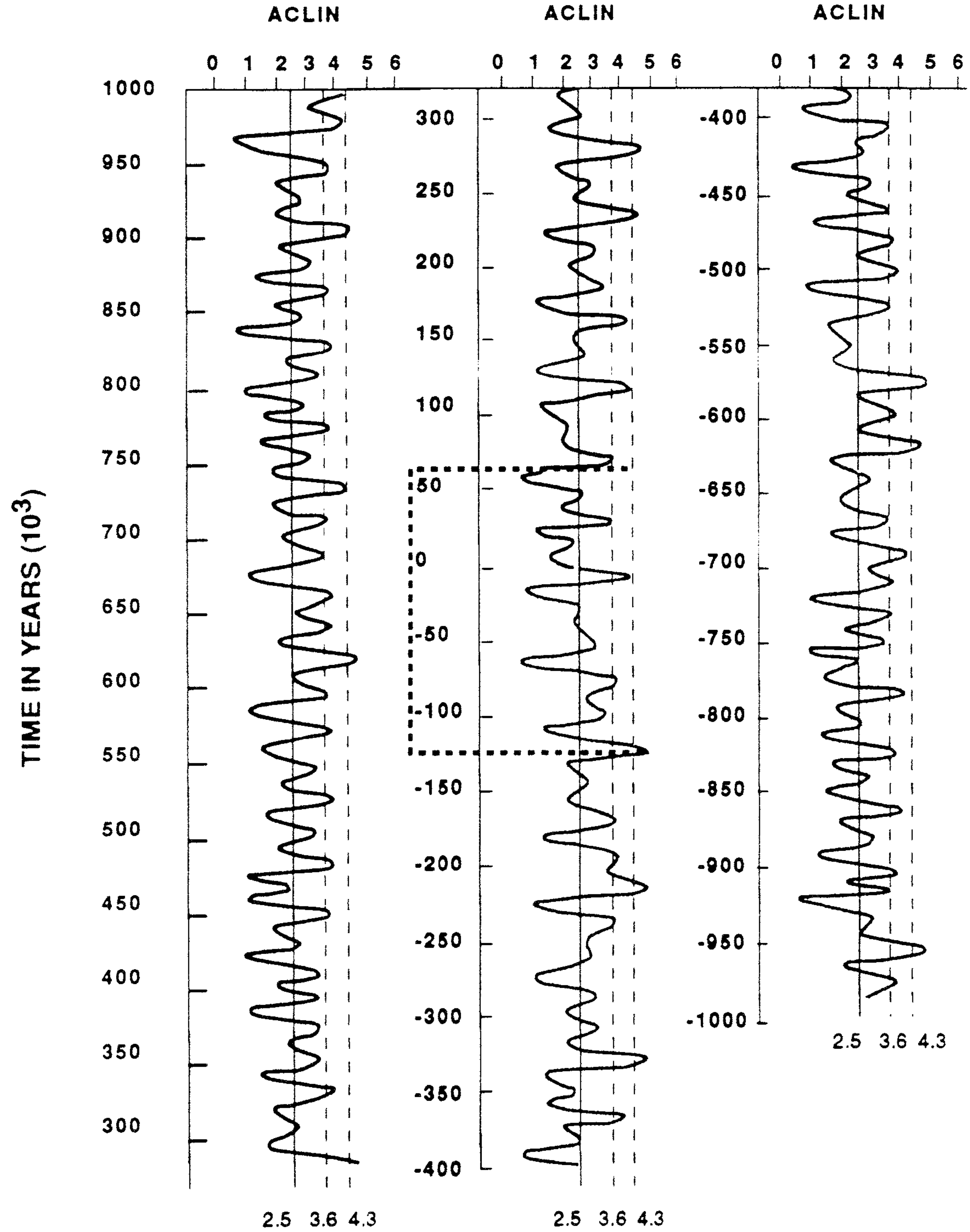

Figure 7.1: Astronomical Climate Index (ACLIN) for the period ±1 Ma (from *[Mathews, 1984]*). The ACLIN curve within the boxed dashed line represents the last glacial cycle and the next 60 000 years;only index values greater than 3.6 correspond to warm periods. This part is detailed in Figure 2.

The astronomical theory is based on the premise that small periodic changes in the earth's orbit around the sun (the Milankovitch orbital parameters) results in variations of the amount of solar radiation reaching the earth, which in turn triggers off episodes of glacial activity. Rather than being stochastic, these irregularities exhibit a distinctive pattern or cycle which constitutes periods of approx. 20 000, 40 000 and 100 000 years respectively.

A more detailed understanding of these long-term palaeoclimatic variations can be obtained, for example, from studying the configuration of loess deposits and by oxygen isotope studies of deep-sea sediments and existing ice masses. Since deposition in deep-sea basins is usually a continuous process, drillcores from such sediments can provide an uninterrupted record of long-term events. For example, isotopic studies of the past approx. 1 Ma from Pacific deep-sea sediments indicate that at least 11 cold phases have occurred. Such studies can even extend back from the Quaternary into the Late Tertiary. One drawback is that because sedimentation is a relatively slow process, short-term details tend to be lost.

Several models exist in the literature which try to unravel palaeoglacial activity with the intention of predicting future glaciations. The SKB/TVO glaciation scenario *[Ahlbom et al., 1991]* bases its future climatic predictions on the ACLIN (Astronomical Climate Index; see *[Matthews, 1984; and Kukla, 1979]* and the *[Imbrie and Imbrie, 1980]* models. The former is mainly related to the Milankovitch orbital parameters, calibrated to the past marine climate, and the latter relates the Milankovitch orbital parameters to six radiometrically dated events in the past. The ACLIN model of ± 1 Ma (Figure 7.1) categorizes climate into interglacial conditions (warmer periods with a climate similar to present-day Sweden; >4.3 indices in Figure 7.1), temperate interstadial conditions (temporary warmer periods within a glacial period with a climate similar to present-day Greenland or Antarctica; 3.6-4.3 indices), interstadial conditions (somewhat cooler than "temporary interstadial"; 2.5-3.6 indices) and stadial/glacial conditions (cold periods with a large build-up of ice sheets; <2.5 indices). The model suggests a regular occurrence of stadials or glaciations in the order of 40/Ma. Figure 7.2 details the next 60 000 years suggesting that present conditions conform to the final stages of a true interglacial. From now to the next interglaciation (approx. 125 000 years) the climate is expected to progressively become colder with a first temperature minimum expected around 5 000 years, although true glacial conditions are not expected to occur until approx. 23 000, 60 000 and 100 000 years; interstadial conditions will prevail between these periods.

The *[Imbrie and Imbrie, 1980]* model (Figure 7.3) is valid only for the northern 65° latitude. It is based on seawater oxygen isotope variations (as can be derived from deep-sea sediments and existing ice masses) which reflect past glacial epochs and is particularly good in simulating the last 350 000 years of climatic change. In common with the ACLIN model, a gradual change to glacial conditions will occur from now on with a maximum at 23 000 years; further glacial periods are predicted at approx. 63 000 and 100 000 years. No initial cold peak at approx. 5 000 years was predicted.

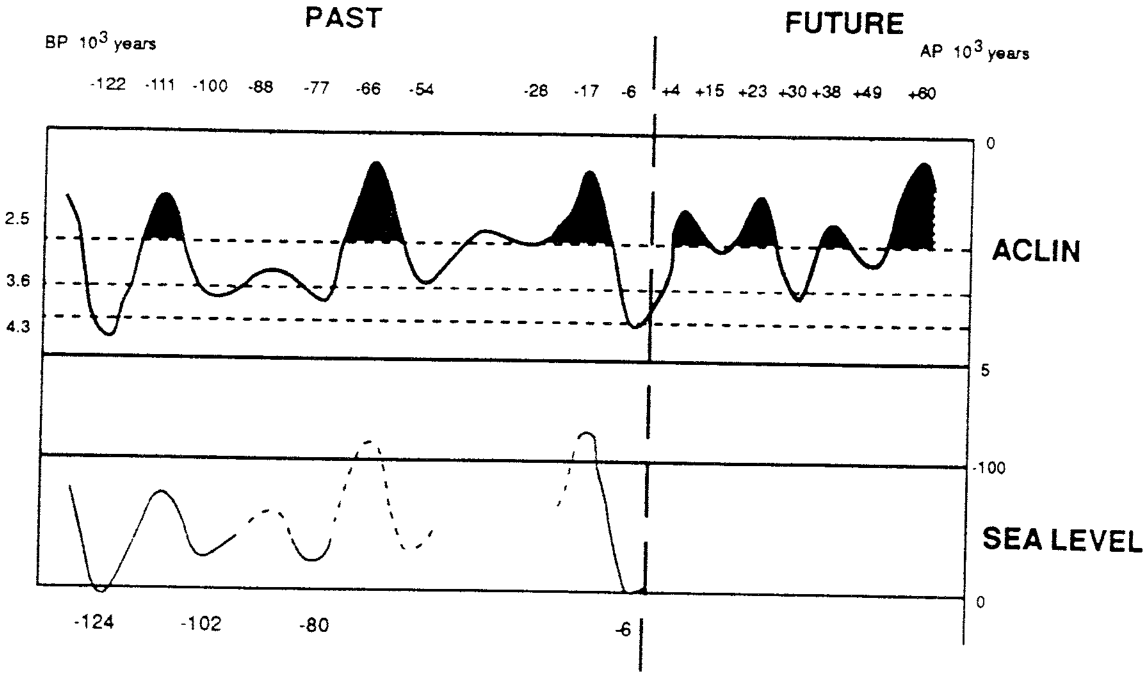

Figure 7.2: Above, the last glacial cycle and the ACLIN projected climate for the next 60 000 years; below, the world sea-level (from *[Mathews, 1984]*).

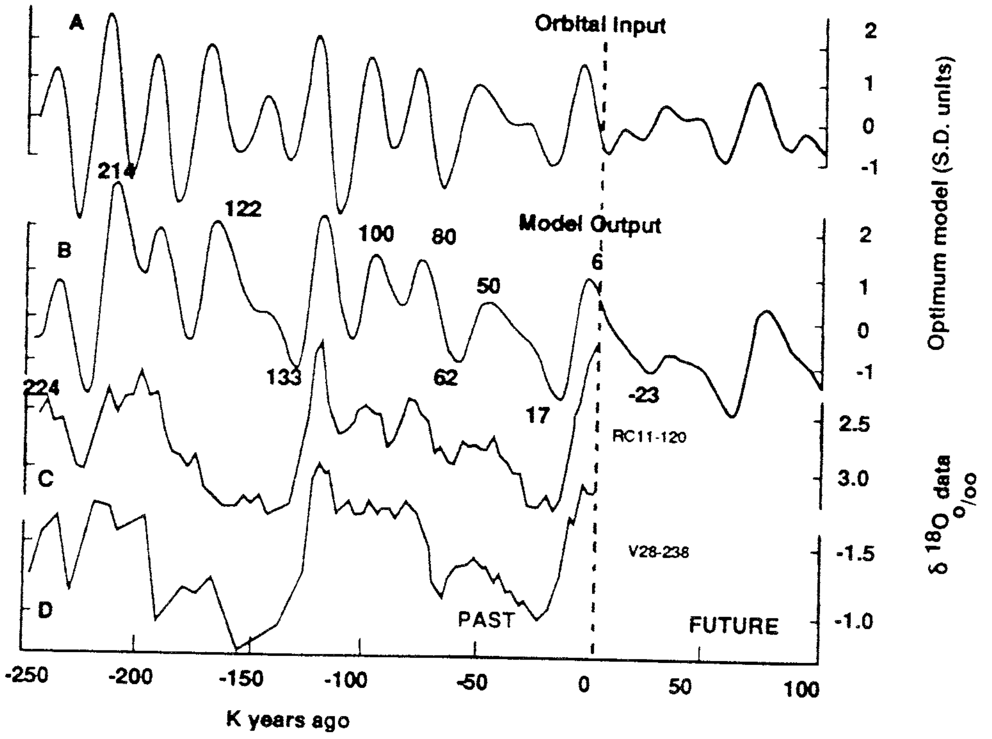

Figure 7.3: Input and output of the *[Imbrie and Imbrie, 1980]* response model compared with isotopic data on climates of the past 250 000 years. A=orbital input; B=model output; C=oxygen isotope curve (Indian Ocean); D=oxygen isotope curve (Pacific Ocean).

It is topical at the moment to be concerned about anthropogenic influences such as the "greenhouse effect" and their potential ramifications on future climatic effects. *[Imbrie and Imbrie, 1980]* assume that the present rise in CO_2 might delay the onset of the next cooling climatic phase by as much as 2 000 years, thus predicting the warmest "superinterglacial" of all time in the near-future. Other researchers believe this anthropogenic period to extend to some tens of thousands of years. Seen in the long-term perspective of waste disposal, however, it is highly likely that the climate will once again respond to the Milankovitch variations and consequently return to predictability.

In summary, even when considering other models linking palaeoclimate with the Milankovitch variations (e.g. *[Calder, 1974; Weertman, 1976; Berger et. al, 1981; Kukla et al., 1981; Oerlemans and Van der Veen, 1984]*), all are basically in agreement with a major change to glacial/stadial conditions at approx. 60 000 years, similar in magnitude to the last glacial maximum with a duration of 20 000-25 000 years. There is also general support for a 20 000 years glaciation, but only one model *[Berger et al., 1981]* indicated a glaciation around 5 000 years.

The SKB/TVO scenario *[Ahlbom et al., 1991]* bases its concept on the assumption that smaller or larger glaciations will occur at approx. 5 000, 20 000 and 60 000 years, and that interglacial conditions (i.e. similar to present-day conditions) will not become reestablished until approx. 75 000 years. At the earliest, man will not resettle in Fennoscandia until after approx. 5 000 years, assuming that a glaciation will occur at this time.

7.3 Effects of glaciations

7.3.1 Permafrost, Ice Cover and Erosion

In general, but not always, glaciation is presumed to be preceded by tundra and then permafrost. Permafrost forms extensively when the mean annual temperature is colder than 2-3°C below zero, when there are dry conditions (i.e. insufficient moisture to create major glaciers), and when there is a time lapse before the ice covers the area. As indicated by present-day occurrences of permafrost in Greenland and Siberia, depths of penetration can reach 500 m and take several thousand years to form.

Gradually an accumulation of ice will form over much of northern Fennoscandia. The Quaternary record shows that some 18 000-20 000 years ago a maximum ice accumulation completely covered Fennoscandia extending as far as the continent (present-day N. Germany). However, even further back in time to approx. 30 000-50 000 years, the ice margin is thought to have been more permanently located across southern Fennoscandia and to have been subject to fluctuation over a long period of time.

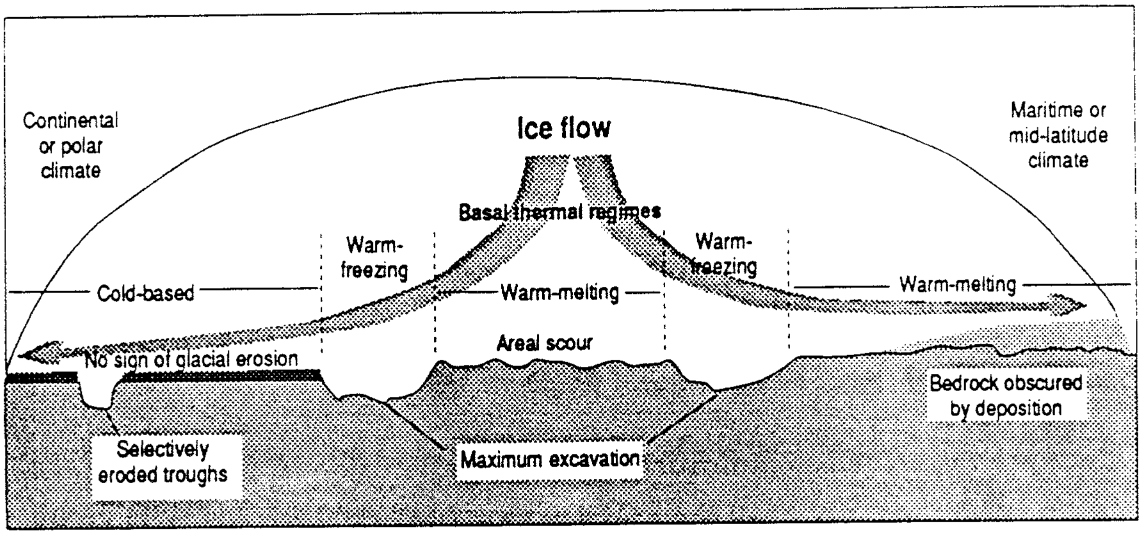

Figure 7.4: Cross-section showing the process of erosion by a continental ice sheet. Left, a cold-based glacier; right, a warm-based glacier. Erosion is most pronounced at points where the base is alternately unfrozen and frozen to the underlying material (from *[Skinner and Porter, 1987]*).

The steady accumulation and formation of the continental ice sheets will eventually result in glacier movement extending over the frozen ground. Two glacier types are recognised; cold-based (dominant type) or warm-based (Figure 7.4). Initially, the glacier will be cold-based as it moves over the frozen ground. However, geothermal heat will gradually melt the permafrost layer (if present) from the bottom up, eventually increasing the temperature at the glacier base. Furthermore, if the pressure exerted at the ice sheet exceeds the pressure melting point (-1.6°C for a 2 km ice thickness), then melting will also occur at the glacier/permafrost interface. In both these cases a warm-based glacier will result.

Warm-based glaciers, because of the lubricative action of the melt water at their base, will move fairly rapidly, compared to the cold-based type. Erosive action will therefore be mostly confined to the warm-based variety, especially when local fluctuations of pressure (and therefore temperature change) will cause alternations of freezing and melting at the glacier base resulting in highly erosive plucking and abrasion processes, accompanied by deposition, occurring at the glacier/rock interface (Figure 7.4). However, it has long been a popular misconception to assume that the ice cover has removed enormous quantities of bedrock material as it slowly ground its way over the Fennoscandian basement. Of course material has been removed, but this has mostly consisted of loose, pre-glacial weathered upper surface. The unweathered bedrock, i.e. much of the pre-glacial Precambrian Shield which has already been scraped clean by earlier major glaciations, has probably been affected to a depth of only a few metres to tens of metres (e.g. an average of 14 m has been calculated for the Canadian Shield and < 10 m for the Fennoscandian Shield), at least in those areas of low relief away from the Caledonides.

7.3.2 Isostatic Movement

Glacially-induced crustal downwarping and rebound during and subsequent to glaciation is basically a simple process. However, calculations are complicated by the fact that ice sheets provide loads of relatively high magnitudes and of such short durations that isostatic equilibrium within geological time-scales are only rarely achieved; time lags of up to 15 000-20 000 years are not unusual. Generally speaking, maximum crustal downwarp under ice is estimated to be 25-30% of the maximum ice thickness, although this is variable and time dependent. After release of the ice load the surface rebound decreases exponentially; uplift in the central parts of the glaciated area may exceed 0.1 m/a with about 0.01 m/year after 10 000 years. Estimates of maximum uplift after the last glaciation in the Fennoscandian region are around 800 m *[Mörner, 1979]*, which is relatively close to the theoretical value assuming that the ice was 3 km thick.

Peripheral to the central downwarped depression will occur an arch or forebulge; this is not expected to exceed a height of 150 m.

7.3.3 Postglacial Neotectonic Activity

Indications of stress-release in the bedrock are reflected by seismic activity, reactivation of established fault systems, rock shattering and sometimes the formation of new faults. These effects are thought to have occurred almost exclusively during ice melting, when the glaciers are retreating and the landmass is rising. This is supported by modern-day analogies with Greenland and Antarctica where glacial/permafrost conditions have been established for a long period of time, and no seismic activity is occurring; stress-release is still being constrained by the ice mass.

For Fennoscandia it has been postulated that during the final stages of ice melt (estimated to have occurred 8 000-9 000 years ago) there were most likely a series of major earthquakes, releasing stresses that had been stored elastically during the glaciation. Since then more normal conditions have returned, characterised by less intense activity. It is difficult to quantify how much of the current strain is released by seismic activity; some estimates put it to only 1/20 000 of the strain now deforming Sweden.

Evidence of postglacial fault movement has been reported from several parts of northern Fennoscandia. This has been well illustrated from one of the study areas in northern Sweden, the Lansjärv neotectonic zone, which can be traced topographically as a distinct scarp for some 60 km *[Bäckblom and Stanfors, 1989]*. The study showed that any new faulting in the area was directly associated with the reactivation of a much older fault plane. Furthermore, examination of the associated Quaternary sediments showed not only ground shock movements associated with reactivation, but that in places only a single displacement of up to 10 m may have occurred. Other neotectonic zones in the area, e.g. the Pärvie fault which extends some 120 km, may have had maximum displacements of up to 15 m. It is probable that these displacements occurred during deglaciation some 8 000-9 000 years ago as the ice front retreated past the subsequent location of the fault scarps.

7.3.4 Changes in Sea-Level

The freezing of large volumes water will initially result in a global lowering of the sea-level. For example, a glaciation extending to Stockholm/Helsinki would give rise to a global lowering of the sea-level by 85 m, and to northern Germany would mean a lowering by 100-150 m. The ice-bedrock interface would lie some 500-600 m below the sea-level. Upon deglaciation, the sea-level would naturally be expected to rise; however, this rise will become somewhat offset by isostatic land recovery which may even exceed the rise in sea-level. Deglaciation at Stockholm/Helsinki is expected to result in a sea-level increase of about 100 m above that at present. It should be noted, however, that these estimations are further complicated by changes in the geodic shape of the earth. During periods of constant ice-masses the global sea-level is assumed constant and the relative changes are due to delayed isostatic crustal adjustments. Rapid sea-level fluctuations, for example due to the sudden breaching of natural ice or moraine barriers etc., can result in the draining of inland lakes and seas (e.g. the Baltic Ice Lake).

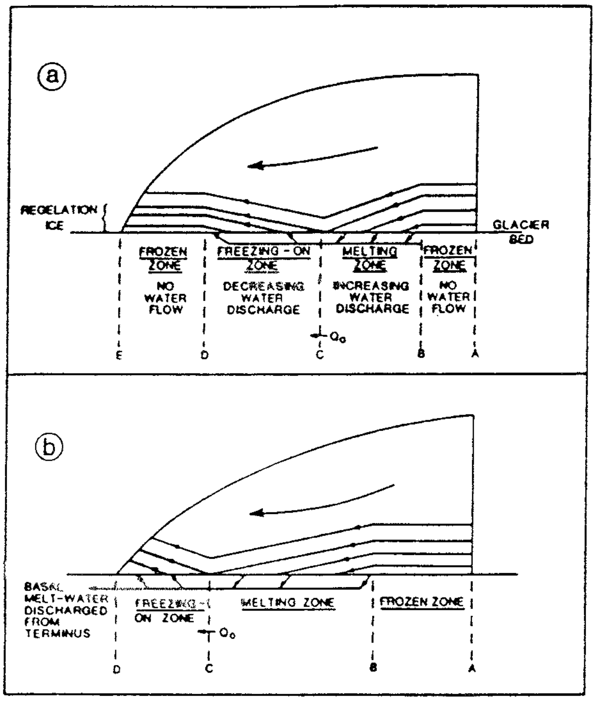

Figure 7.5: An idealised ice sheet showing a complete sequence of possible basal mass-balance (melting or freezing-on) states. Beneath a given glacier there might be zones AB or BC only, or AB-BC, AB-CD, BC-CD, BC-DE, or a repetitive sequence if the bed is highly irregular (after *[Boulton and Spring, 1986]*).

7.3.5 Hydrogeology

Few data exist of hydraulic conditions beneath continental ice sheets or glacier systems. Some boreholes have penetrated the Antarctica and Greenland ice sheets and water has been located at the ice base at a depth of 2 164 m, possibly as a basal layer of the order of 1 mm thick *[Embleton and King, 1975]*. The hydraulic head at the ice base will be a function of the size and pressure exerted by the ice mass at that point. Figure 7.5 illustrates the various stages of freezing and melting that might be expected to occur along the ice/bedrock interface. In the central part the basal temperature will be below the melting point so that hydraulically stagnant conditions will prevail. Beyond is a broad zone of melting (rates estimated to range from 2-50 mm/year), where any discharge will require a substantial piezometric gradient to drive it, thus tending to induce strong groundwater flow in any aquifer. However, permafrost beyond the ice margins may effectively seal off discharge to all or part of these aquifers. This may result in a build-up of subglacial groundwater pressure, increasing instability and surging of the ice sheet or producing extensive hydrofracturing at the glacier/bedrock interface.

If the subglacial rocks or sediments are sufficiently permeable, the subglacial groundwater, driven by the slope of the glacier, will tend to be discharged parallel to the glacier flow. If transmissivity is low, the piezometric gradient will increase to maintain discharge. However, if the potential pressure of the subglacial groundwater rises to equal that of the ice pressure, then discharge will occur at the glacier/bedrock interface through the formation of a tunnel network where groundwater pressures are slightly close to or less than the ice pressures.

7.3.6 Hydrogeochemistry

Under the ice sheet, at the ice margins and at the ice front, alkaline, highly oxidising melt water of low ionic strength and low carbonate content (due to the absence of microbial activity) may access the bedrock to considerable depths (due to great differences in hydraulic head) via deeply penetrating hydraulic fracture zones.

During permafrost formation, fractionation during freezing may give rise to increasingly saline waters *[Boulton and Spring, 1986; Herut et al., 1990]*. This may produce a downward percolating saline front which could extend to substantial depths via density gradients and hydraulically active fracture zones.

Another potential source of saline water is the remobilisation of such waters which presently exist in the bedrock. Present-day saline occurrences, e.g. in the Canadian and Fennoscandian Shield areas, can be found anywhere between 500-3 000 m depth and contain up to 20-30% salt. Remobilisation of these waters can be directly observed today in the Antarctica. Here, where the normal recharge cycle is effectively "frozen" by permafrost, the delicate hydraulic balance between deep saline water and overlying fresh water is upset such that the saline waters migrate to shallower levels and even to the base of the ice sheets. Saline lakes are observed to occur at the ice margins. Following deglaciation the saline waters saturating the upper bedrock horizons will largely be flushed out and exist only at depth, as exemplified today in Canada and Fennoscandia.

Saline water incursion comes not only from depth, but also from marine transgressions as a consequence of ice loading and depression of the bedrock. Isostatic movement would certainly increase the regional hydraulic gradient, thus providing a mechanism for an increased groundwater flow through the repository site. There is some evidence from site investigations (e.g. Äspö) that during the Quaternary, flushing of the bedrock by fresh and saline groundwaters has periodically occurred in southern Fennoscandia.

7.4 Performance Assessment Considerations

Central to the debate on the safety of a radioactive waste repository is the integrity of the host bedrock over long time intervals. Glacial and interglacial periods will undoubtedly put the bedrock under variable stress, and it is the ability of the bedrock to accommodate such stress that provides the crux to repository safety.

The reactivation of existing fractures versus new fracturing during deglaciation is an important subject of debate within waste management circles. If it can be conclusively shown that periods of glaciation in the Quaternary have produced new crustal fracturing to repository depths, rather than reactivation along older faults, then serious reevaluation of some of the performance safety assumptions may have to be considered. Present evidence, however, shows that reactivation along ancient fault zones is the dominant mechanism resulting from deglaciation stress-release; any new faults tend to occur adjacent to, and are subsidiary to, the reactivated faults. This supports present repository conceptual models which consider that any crustal movement will be "buffered" by readjustment within and along preexisting bounding fracture zones (i.e. "deformation barriers"), rather than affecting the rock block mass which houses the repository.

Changes in hydraulic conductivity and groundwater chemistry would appear to pose the greatest threat to repository safety, although these affects should, once again, be mainly confined to existing hydraulic pathways in the far-field, i.e. the same structural features which bound the repository. However, little is known about the time required to saturate the repository environment with groundwaters of different chemistry, particularly in the near-field environs. Such changes might be expected, especially if an increase of groundwater flow rates through the repository area is to be anticipated, resulting from changes in the regional hydraulic gradient due to isostatic recovery, or, even more so during deglaciation when the ice margin is located above the repository. Evidence in Fennoscandia since the last glaciation shows that marine-derived waters have been effectively flushed out of large volumes of typical repository-type bedrock and replaced by fresh water, and vice versa. This has undoubtedly happened at each glaciation and over periods of time well within the projected life-span of the repository.

The exact nature of the hydrogeochemical changes anticipated in the repository during glacial conditions are still to a large extent speculative. There are two major concerns about the chemical stability of the near-field engineered barriers: a) the incursion of oxidising, low ionic strength groundwaters, and b) the incursion of saline groundwaters.

Highly oxidising, alkaline melt waters of low ionic strength and low carbonate content are expected to form under the ice sheets and at the ice front. Combining groundwater access via deeply penetrating conductive fracture zones with extensive shaft seal failures, it is conceivable that these oxygenated waters could reach repository depths. The penetration of such waters over long periods of time might serve to diminish the overall redox buffering capacity of the bedrock due to the large-scale oxidation of mafic minerals, and also dissolve calcium minerals such as calcite, gypsum, anhydrite and fluorite which would increase the anion concentration of bicarbonate, sulphate and fluoride etc. in the near-field, thereby increasing potential radionuclide mobility. Furthermore, an increase in calcium availability due to these reactions would allow it to participate in ion-exchange reactions with the bentonite buffer material converting the sodium bentonite to the calcium variety which has a lower swelling pressure and thereby sealing capacity. However, it is well to point out that no dramatic present-day subsurface changes in bedrock chemistry can be directly related to the last deglaciation, at least not to any marked depth.

Saline waters, whether marine in origin or from deep in the bedrock, may also have a detrimental influence on radionuclide mobility and on the stability of the near-field barrier system as a whole. Even though pH, redox potential, and the complex-forming anions largely determine transportation kinetics, the introduction of saline water into the repository area (during and subsequent to glaciation) will serve to increase the number of competing ions in solution. Some radionuclide ions such as Cs^+ and Sr^{2+}, which are mainly sorbed by ion exchange unto the minerals, are sensitive to salinity. Their retention will be reduced in a saline environment. Furthermore, the bentonite itself being an ion-exchanger is influenced by the salinity, for example, properties such as swelling pressure and pH can be affected. Calcium-rich saline groundwater will tend to lower the swelling pressure in a sodium bentonite with an initial density of 1.6 g/m^3 or below. Increasing salinity in a bentonite water mixture liberates protons from the bentonite which are exchanged for positive ions. Dilute or ion-free water will result in the contrary, i.e. a pH increase. Natural bentonite contains calcium carbonate which participate in pH-buffering reactions in the clay and can also act as an internal source of calcium and carbonate ions.

With regard to canister stability, saline water contact in itself could be so marked that the existing thermodynamic boundary conditions for only oxygen and sulphide reactions to occur, would no longer be applicable, e.g. if there was an appreciable increase in chloride together with a low pH. However, most saline groundwaters studied seem to be characterised by high pH (7-8), rather than values of 4 and less required for corrosion. Moreover, as stated above, the bentonite will act as a pH-buffer. Therefore, an increase in salinity is not expected to cause an oxidation of the copper canister by water. This would support the conclusion that the copper canister is stable.

Saline waters can enter the bedrock at several stages of the glaciation/deglaciation process: permafrost, ice accumulation and deglaciation. During permafrost formation groundwater freezing can produce a downward percolating saline front which could reach repository depths if the hydraulic conditions are conducive. Furthermore, assuming canister leakage, permafrost may also result in a concentration of radionuclides in the groundwater beneath, or within, the permafrost zone, which may subsequently be released as a concentrated "pulse" when thawing takes place. It has also been speculated that gas derived from within the rock mass may become frozen as clathrates (gas hydrates) within the permafrost zone or trapped beneath as a gaseous "cushion". Thawing may result in an explosive release of the contained gases. At the moment, however, these geogas effects are not considered to be a major problem because of the small volumes of dissolved gas presently detected in groundwater.

Saline groundwater migration from depth to higher (repository) bedrock levels can presently be observed in Greenland and Antarctica. In addition to being normally NaCl-rich, these saline groundwaters can also be very Ca-rich and thus pose a direct problem to the stability of the bentonite. However, deglaciation is perhaps the most dynamic stage for groundwater mixing and near-field instability to occur. It is at this stage that ancient fault reactivation, whilst not mechanically threatening the repository, may result in a general increase of hydraulic conductivity around the repository site coupled with changes in groundwater chemistry. Greater bedrock conductivities will therefore facilitate the influence of other related deglacial processes such as isostatic recovery and changes in sea-level. With the lowering of the sea-level due to land uplift, marine-derived saline waters will be flushed out and fresh water will increasingly come into contact with clay minerals previously in contact with marine waters. This will lead to the ion-exchange of sodium for calcium and thereby increasing calcite solubility. Transport of these waters to depth may also be facilitated by deep hydraulic fracture zones enhancing both groundwater mixing and repository near-field reactions.

The positioning of the repository in relation to the predicted extent of glaciation could be of importance. Assuming a coastal location which has been substantially covered by an inland ice sheet, crustal downwarping will exceed the drop in sea-level causing a submarine environment for the repository during deglaciation. Any repository leakage to the bedrock surface will, in this case, be minimised by sea water dilution, at least until further isostatic recovery will raise the repository once again above sea-level. In contrast, assuming a higher, more inland repository location, or a coastal location near the maximum extension at the ice margin, the isostatic downwarping will not result in a submarine environment. Any radionuclide leakage to the biosphere in this scenario will thus be of a much greater direct threat, although some dilution should also occur in association with glacial outwash rivers and lakes.

At our present stage of knowledge, however, radioactive leakage during deglaciation is not considered a major problem. Few if any people will inhabit these regions and strong dilution of any leaking waste products will minimise any doses thereof.

8. Analogues for Construction Materials

8.1 High-level Radioactive Waste

8.1.1 General

The near-field barriers are an important part of the repository system, And to analyse their performance constitutes a central part of the overall performance assessment. The near-field is usually thought of as comprising the engineered barriers that are in contact with, or located in the immediate vicinity of, the waste. The safety-related functions of the engineered barriers are to contain the radionuclides in the waste during the initial disposal period so that comparatively short-lived radionuclides decay, and also to help limiting the release rates of the radionuclides from the waste once the containment (the canister) has been penetrated. This is achieved by placing the waste in a canister of sufficient durability and by surrounding it by a buffer material that protects the canister both from mechanical forces (e.g. due to rock movements) and from flowing groundwater.

In the following account the engineered barrier system is regarded as consisting of the matrix of the waste form (UO_2 in the case of spent fuel or borosilicate glass in the case of HLW from reprocessing), a canister containing the waste form, a clay buffer surrounding the canister, and the backfill in tunnels and shafts which consists of a mixture of clay and sand. Issues related to concrete stability are treated in the Section 8.2 dealing with low- and intermediate-level waste although it cannot be excluded that concrete will also be used in HLW-repositories.

The properties and behaviour of the materials used in the engineered barrier system must be demonstrated over very long time-scales in order to assess the safety of a repository. Various models are used to extrapolate the laboratory characterisation of barrier behaviour. However, to validate these models, which relate to short-term material degradation over hundreds to thousands of years, is beyond conventional engineering experience. Validation, even though being only partial, is therefore sought by the natural analogue approach.

8.1.2 Waste Form

The features of the waste form which are of interest in performance assessment essentially relate to the variability of the physico-chemical properties of the waste with time, i.e. chemical, thermal, mechanical and radioactive properties *[Petit, 1990]*. Chemical alteration of the matrix will lead to the release of radionuclides and several different mechanisms may be envisaged. For example, dissolution of the UO_2-matrix will of course release radionuclides embedded in the solid. Another possibility is oxidation of UO_2 to form higher uranium oxides with contrasting crystalline structures, i.e. if oxidation progresses beyond U_3O_7 to U_3O_8 or UO_3. Elements bedded in the original matrix can thus become released and thereby coming in contact with the aqueous phase. For the very soluble radionuclides elements such as Sr, the matrix transformation would in principle be a release rate determining step. For less soluble species such as Pu, the solubility of the oxide will determine the release rate. Mechanical fracturing of the waste can increase the surface area available for alteration, and radioactive effects can lead to radiation-induced dissolution transformation to other solid phases by corrosion reactions. Because of the major importance of liquid/solid reactions in waste form stability, solution properties must also be considered, i.e. Eh, pH, solubility and speciation of radionuclides and the influence of colloids, organics and microbes *[Petit, op. cit.]*.

Spent nuclear fuel, rather than vitrified waste (i.e. borosilicate glass) or natural mineral-based ceramics (i.e. "Synroc or monazite/sphene), is the preferred concept for both the SKB and TVO high-level radioactive waste programmes. The major waste component in spent fuel is UO_2 ($>95\%$), together with matrix impurities such as nuclear fission products, actinides and actinide daughters contained in the fuel. The transuranic elements probably substitute for uranium in the UO_2 crystal lattice, and the fission products are partly contained within the lattice and partly on the crystal margins. Naturally occurring uraninite or the less pure variety of pitchblende are commonly considered analogous to spent fuel, containing in some cases up to 90% UO_2; but important dissimilarities do occur. For example, matrix impurities in natural material often include traces of rare-earths (e.g. La, Ce, Gd), Th and Y, and greater amounts of Ca, Fe and Si; the largest discrepancy in composition is often the content of radiogenic lead (sometimes 25 wt.% and more) which is a reflection on the age of the uraninite/pitchblende phases. There are also important differences in morphology between UO_2 minerals and spent fuel. Uraninite has been precipitated from a hydrothermal solution and pitchblende at lower hydrothermal temperatures and also at ambient temperatures from groundwater solutions. Fuel pellets, on the other hand, have been manufactured by pressing and sintering of UO_2 powder, and spent fuel has resulted in these pellets being subjected to an intense history of high temperature and a very large thermal gradient from the centre of the pellet cylinders to the fuel cladding surface. The material is microcrystalline and ceramic like and the thermal stress in the reactor results in cracking and fracturing of the pellets. Some radionuclides have migrated in the fuel and these tend to become enriched along the cracks and pellet surfaces, and maybe also at grain boundaries. Furthermore, the crystal structure of spent fuel differs in that it may be somewhat disorganised by the intense radiation field, and hence be more soluble. Despite these differences, the study of natural uraninite ore and its surroundings provide important clues to the predicted long-term behaviour of spent fuel in a repository environment.

Laboratory studies on the stability of spent nuclear fuel, critical for understanding the initial, or short-term corrosion behaviour during temporary storage and initial permanent disposal, are well documented (e.g. *[Johnson and Shoesmith, 1988]*). Mechanisms of spent fuel alteration have essentially been identified through laboratory experiments conducted on pure UO_2 *[Bruno et al., 1986; Lahalle et al., 1989; Sunder et al., 1988]*. However, predicting the behaviour of fuel over thousands of years falls outside the scope of experimental extrapolation. As pointed out by *[Finch and Ewing, 1991]*, only by an integration of short-term spent fuel studies with long-term analogue studies can a confident assessment of spent fuel behaviour be possible.

Laboratory experiments on spent fuel stability show that dissolution is slow to minimal under any conditions which approach those expected in and around a repository; UO_2 simply dissolves more rapidly under oxidising as compared to reducing groundwater conditions. The high stability of uraninite under reducing conditions is attributable to the very low solubility of U(IV), estimated to be $< 1 \bullet 10^{-9}$ Mol/kg *[Bruno et al., 1986]*. Laboratory studies also show that UO_2 dissolution is sometimes accompanied by the formation of uranyl phases on the fuel surface. There are indications of schoepite being the solubility limiting phase for uranium in UO_2-leaching experiments under atmospheric conditions.

Analogues addressing the stability of natural uraninite/pitchblende under varying redox conditions show that the dissolution rate under oxidising conditions was reduced by the presence of thorium, lead and REE impurities, and that age did not appear to influence the dissolution rate *[Grandstaff, 1976]*. *[Finch and Ewing, 1989]* reconstructed the breakdown of uraninite under oxidising conditions present at Shinkolobwe, Zaire, as a natural analogue for the corrosion of spent nuclear fuel in contact with oxidising groundwaters. They observed that uraninite initially transforms to Pb-U oxide hydrates and then to uranyl silicates if sufficient Si is present in solution; an overall reduction in grain-size was noted as alteration proceeds. *[Smellie and Rosholt, 1984]* showed that even though uranium mineralised fractures in crystalline rock (50-130 m depth) had been subject to water-rock interaction processes, the non-oxidative groundwater environment had preserved the integrity of the uraninite for most, if not all, of its 1.75 Ga existence, including the last 0.5 Ma when it has been closest to the earth's surface. Furthermore, the Cigar Lake analogue study indicates that at repository depths there is no convincing textural or chemical evidence of significant ambient low temperature removal of uranium under reducing groundwater conditions from the massive uraninite-dominated ore body since its formation some 1.3 Ga ago. As long as conditions remain reducing, the element is practically immobile; measured concentrations in groundwater are around 1 ppb, similar to UO_2 solubilities measured in the laboratory.

In the context of spent fuel stability, much attention has been given to the Oklo natural reactors which underwent criticality some 2.0 Ga ago resulting in the concentration of nuclear fission products, actinides and actinide daughters associated intimately with uraninite which crystallised from pitchblende during fission. Early geochemical studies on several reactor zones are documented by the IAEA *[IAEA, 1975, 1978]*. Since then much additional data have become available (see e.g. *[Loss et al., 1989; Curtis et al., 1989; Brookins; 1990; Holliger, 1991]*). The general stability of the uraninite, both from hydrothermal effects during criticality (estimates range from 140° to 450°C) and at ambient groundwater temperatures throughout geological time since then, is supported by the following conclusions summarised by *[Jakubick, 1986]* and *[Brookins, 1990]*:

- despite a high fission density, no trace of metamictisation (distortion of the crystal lattice due to radiation) of the uraninite was detected,

- the ^{239}Pu produced remained and decayed to ^{235}U in the uraninite matrix, and

- the fission products forming either metallic inclusions (Rh and Pd) in the host uraninite, or oxides stable in the uraninite structure (Th, Pu, REEs, Bi, Te, Y, and Nb), where retained within a few microns.

The analogy between spent fuel and Oklo uraninite is not, however, absolute; three important differences exist:

1) Oklo uraninite contains lower concentrations of fission products than spent fuel.

2) The maximum temperatures achieved at Oklo (up to 450°C) are lower than in an industrial reactor and, consequently, the fission products in the Oklo uraninite will not have undergone fractionation to the same extent as spent fuel.

3) Oklo uraninite is better preserved than the UO_2 comprising the spent fuel rods because of a less complete nuclear reaction, thus rendering the reaction products less susceptible to groundwater attack.

In uranium deposits which have not achieved criticality, there exist in the natural environment a limited number of radionuclides that have stable isotopes suitable for study; multivalent radionuclides such as Tc and Pu are, however, much more problematical with respect to suitable chemical analogues. Nuclear processes do, never-the-less, occur in nature with the production of trace amounts of ^{99}Tc and ^{239}Pu in association with high-grade uranium deposits. For example *[Curtis et al., 1987]* have studied ^{99}Tc and ^{239}Pu from the Koongarra uranium deposit, Australia and *[MacKenzie et al., 1990]* report measurements of ^{239}Pu from the Osamu Utsumi uranium mine, Poços de Caldas, Brazil. These studies have shown that at Koongarra the uranium minerals have effectively retained ^{99}Tc and ^{239}Pu on a time scale of 1 Ma, and at the Osamu Utsumi mine ^{239}Pu has been retained on a time scale of 10^5 a.

8.1.3 Canister

The function of the canister is to isolate the spent fuel from groundwater contact for designated time periods ranging from thousands to hundreds of thousands of years depending on waste composition (reprocessing waste or spent fuel) and design goal. Copper, because of its thermodynamic stability in deep, reducing groundwater, is the reference canister material in the SKB and TVO programmes to encapsulate the spent nuclear fuel. Recently TVO have developed a more structurally stable alternative comprising a copper canister with an inner carbon steel support *[Salo and Raiko, 1989]*; this is presently under review. The upper (oxidising) limit for copper stability is linked to the formation of cuprite (Cu_2O), i.e. dependent only on the Eh and pH, and the lower (reducing) stability limit is linked to the presence of dissolved sulphide ions, in addition to the Eh and pH, to produce chalcocite (Cu_2S).

Generally, the life span of the copper canister depends on metal purity and the quality of the engineering (e.g. canister sealing), together with the composition of the groundwater (e.g. sulphide content) which it will ultimately come in contact with. Confidence in the canister is therefore based on thermodynamic considerations, the extent of available laboratory data, and the fact that the groundwater chemistry will be stable at repository depths due to the strong buffering by the composition of the bedrock mass. General corrosion rates (0.025-1.3 μm/a) calculated from both historical and archaeological copper artifacts found in a wide range of wet/dry and oxic/anoxic environments *[Chapman et al., 1984]* demonstrate the long-term durability of copper, consistent with thermodynamic considerations. For example, assuming only general corrosion and a 10 cm thick copper canister, the resulting penetration time would be between 80 000 a and 4 Ma.

Canons from the Swedish 17th century warship Kronan sunk in the Baltic Sea constitute another interesting analogue to copper canister corrosion. The copper rich guns (96.3 % Cu) were salvaged after more than 300 years on the bottom of the sea, where some of them were submerged in the clay sediments. Outside northern Öland, where the ship sank, the seawater is brackish. Copper, clay and saline water are analogues to typical components of a repository, e.g. KBS-3. From this study the general conclusion was that copper corrodes very slowly in this environment. Less than a cm would have been corroded after 100,000 years according to the observed reaction rate *[Hallberg et al., 1988]*. More detailed assessments were difficult to make because the guns had already been covered with a skin of corrosion products (eg tenorite) before the ship sunk. The identified copper corrosion products cuprite and malachite indicates mainly oxic corrosion. Bacteria may have been involved in the observed reduction of tenorite (CuO). Copper sulphides were not reported.

Owing to the predicted low supply of oxidants expected to reach the canister (because of reducing repository conditions), local corrosion attack (i.e. "pitting") is considered to limit the life of the canister should corrosion be the predominant mechanism. Since the theoretical basis for the "pitting factor" (an important criterion which can determine the potential extent and depth of corrosion) is weak, important support for this process has been provided by analogue studies (e.g. *[Johnson and Francis, 1980; Bresle et al., 1983; Hallberg et al., 1984]*). These studies have involved native copper (up to millions of years), archaeological artifacts (2 000-300 a) and earth electrodes (< 100 a) for lightning conductors, all of which lend credence to copper stability in some chemical environments. A fairly pure copper axehead, discovered in a shallow anoxic marsh area in Suomussalmi, Finland showing only superficial corrosion, has been dated to ca. 2 000 BC.

Safety assessment calculations for the KBS-3 concept involved a pitting factor of 5 (as observed from archaeological materials, e.g. the Kronan cannon described by *[Hallberg et al., 1988]*) and an unfavourable case of 25 (as observed from the exposure of copper in soil). All available evidence from natural occurrences and archaeological artifacts showed that a pitting factor of 5 was more realistic, concluding that the proposed copper canisters should last for at least 1 Ma.

One of the best natural analogues of copper is the existence (i.e. preservation) of massive native copper deposits on the Keweenaw Peninsula, Michigan, USA *[Crisman and Jacobs, 1982]*. These deposits, of Precambrian age (around 500 Ma), occur within a series of volcanic basaltic lava flows interbedded with conglomerates; the copper principally occurs either as amygdaloidal infillings in the lava flows or as interstitial fillings in the conglomerates. The massive deposits are the result of widespread hydrothermal remobilisation of trace amounts of copper derived from silicate minerals of underlying formations. Deposition of the native copper resulted from the interaction of these metalliferous hydrothermal solutions upon contact with the reducing, sulphur-poor basaltic lavas and conglomerates.

The native metal has a very low impurity content (99.998 wt.% Cu) and has been exploited for some 4 000 a. Copper boulders exist as glacial erratics deposited during glacial melting 8 000 a ago; since then they have been subject to large climatic extremes which have only served to produce thin surface oxide coatings. By comparing abraded faces (resulting from glaciation) with unabraded faces (pre-glaciation surfaces), *[Johnson and Francis, 1980]* found that the former was characterised by a very thin oxide layer (0.07-0.60mm) and the latter by appreciably thicker layers (up to 2mm). Extrapolation of these data *[Chapman et al., 1984]* indicate time scales exceeding 1 Ma to oxidise a 10 cm thick copper canister under such extreme conditions.

Other disposal concepts plan to encapsulate high-level radioactive in massive steel overpacks. However, as steel is a relatively recent technological alloy, natural analogues are mostly limited to geological or archaeological artifacts (e.g. *[Hellmuth, 1991]*). Iron meteorites and archaeological artifacts comprising iron or iron alloys have been categorised by *[Johnson and Francis, 1980]*, native iron occurrences have been studied at Disko Island, Greenland, by *[Bird and Weathers, 1977]* and archaeological artifacts such as a horde of Roman iron nails discovered at Inchtuthil, Scotland, are described by *[Pitts and St. Joseph, 1985]*. Although no useful analogue information on localised corrosion (i.e. pitting) of iron or steel is available, the most appropriate data indicate a total corrosion time for a Nagra-type (25 cm thick canister walls of mild steel *[Nagra, 1985]*) container to be anything from 10 000 to 250 000 a.

8.1.4 Bentonite Buffer

When placed in the deposition hole, located in the floor of the access tunnel, the copper canister is isolated from the rock by blocks of buffer material which consist of highly compacted pure sodium-montmorillonite rich bentonite clay. These blocks, when in contact with water, swell to a homogeneous mass filling up any residual voids in the deposition hole. Thus, the function of the buffer material is to: a) constitute a mechanical and chemical zone of protection around the canister (i.e. a zone of low hydraulic conductivity, of plasticity to accommodate minor deformation, of bearing capacity, and of long-term thermal stability), b) limit the inward percolation of potentially corrosive substances from the groundwater to the canister surface, c) in the event of canister penetration limit the dispersion of leached radionuclides from the canister out into the bedrock, and d) filter fine particulate and colloidal material that may form.

One of the major problems regarding the use of bentonite is the conversion of smectite clay (which includes Na-bentonite) to illite clay during increases in temperature, pressure and water circulation (i.e. potential source of exchangeable K^+ for Na^+). Illite is less suitable for containment because of a lower swelling pressure and reduced plasticity. A drop in swelling pressure in the backfill mass can lead to the formation of voids and cracks resulting in open connections for groundwater flow. Analogue studies of bentonite stability have therefore involved long-term naturally occurring scenarios of clay alteration (mostly diagenetic and contact metamorphic processes) in different geological and thermal environments (e.g. *[Roberson and Lahann, 1981; ENEA, 1982; Pusch, 1983; Brusewitz, 1986; Petit, 1986; Pusch et al., 1987; Pusch and Karnland, 1988; Petit, 1988]*). For example, bentonite stability under laboratory conditions, within the temperature range of 100-130 °C is not well established. Use has therefore been made of a natural occurrence of bentonite, located at 525 m depth and dated to around 450 Ma, described from Hamra, Gotland, S.E. Sweden *[Pusch and Karnland, op. cit.]*. Here, during a period of at least 10 Ma, the bentonite had been subjected to temperatures of 110-120°C and still there is no evidence of any adverse effects on the buffer properties. A study of illitisation at higher contact metamorphic temperatures (105-240°C) indicates transformation to 40% illite over a period of 3.4 Ma *[Kamei et al., 1990]*. These support earlier observations from Kinnekulle *[Pusch, 1983; Brusewitz, 1986]* which showed that even though there was substantial illitisation at temperatures up to 110°C (maintained for several hundreds of years), there was no obvious loss in plasticity or expansion properties on hydration. These analogue observations thus play an important role when stating that the thermal pulse predicted in the deposition hole will not result in any deterioration of the clay barrier.

Investigation of samples from different clay deposits have also indicated another phenomenon that implies a certain brittleness and loss of swelling properties of smectite-rich clays *[Push, 1983; Push and Karnland, 1988]*. This is referred to as cementation and is probably caused by precipitation of silica or, alternatively, iron hydroxides in the clay. Swelling and plasticity are the most important properties of the clay as a buffer between the high-level waste canisters and the walls of the deposition hole. However, it was demonstrated that the change in clay properties due to the cementation effect is not irreversible. Mechanical breakage induces renewed hydration and swelling *[Push et al., 1987]*.

In the context of hydraulic and elemental retardation properties, it is worth mentioning the observations from the Cigar Lake uranium deposit and the Oklo uranium reactor occurrence, both of which are surrounded by an envelope of clay, mostly illite in composition. These clay layers have demonstrated their effectiveness, both as a hydraulic barrier against water circulation (Cigar Lake and possibly also Oklo) and a barrier to fission product migration (Oklo). Another examples of hydraulic isolation by clay due to low hydraulic conductivity is the clay preserved forest at Dunarobba, Italy *[Ambrossetti et al., 1992]*.

In summary, analogue studies of bentonite-type clays, representing a wide range of physical and chemical properties, show a consistent picture of alteration rates below those assumed for the safety analysis. At ambient repository temperatures (less than 80°C), they indeed suggest that the final maximum alteration will be well below 30%, and hence the assumption in the safety analysis that the bentonite properties will remain constant for at least 1 Ma, seems to be well justified.

8.2 Low- to Intermediate-level Radioactive Waste

8.2.1 General

These wastes are packaged in steel drums and in concrete or steel containers. In some of these wastes, for example, ion exchange resins from the primary circuits, are solidified in a cement or bitumen matrix. The highest activity waste in the Swedish SFR and Finnish VLJ repositories will be isolated in a concrete silo. In SFR the voids between the containers are filled with a bentonite buffer and in VLJ crushed rock is used as backfill, forming a hydraulic cage around the silo. The remainder of the waste will be stored in rock caverns (SFR) or in another silo. Following final sealing and saturation of the repository, the near-field groundwater chemistry is predicted to become very alkaline and reducing. In this environment, the stability of concrete/steel constructions, the durability of the cement and bitumen matrices solidifying the wastes, and the nature of the breakdown products that may possibly enhance the solubility and subsequent transport of radionuclides, are therefore critical factors to the performance safety assessment of such repositories.

8.2.2 Concretes and Cements

The long-term integrity of repository construction materials such as cement, steel and bitumen in a highly alkaline groundwater environment is largely surmised only from laboratory-based modelled simulations. In the short-term, two analogue approaches have been used to study the durability of concretes and cements: a) archaeological building materials (hundreds to thousands of years), and b) industrial building material (tens to hundreds of years). The major problem with the archaeological material analogy is that modern concretes are composed of portland cement (mainly calcium silicates with little free lime) with chemical and physical properties much more extensive than ancient lime-based cements. However, some of the ancient cements also contain CSH (Calcium Silicate Hydrate) compounds, formed due to specific conditions of the cement preparation (e.g. *[Petit, 1988, 1990]*), which are the main hydration products of modern-day portland cement. These CSH compounds have consequently served to stabilise and preserve these ancient cements for up to 2000 years. It follows that with to-day's technology, CSH compound-bearing concretes should exhibit a durability even better than indicated from archaeological materials.

The potential use of archaeological analogues for assessing the stability of cement binders is best demonstrated by construction samples studied from Hadrian's Wall in northern England *[Jull and Lees, 1990]* and from the Gallo-Roman baths in southwestern France *[Rassineux et al., 1989]*. These studies *[Petit, 1990]* confirm that the long-term carbonation of hydrosilicates is the dominant alteration mechanism of the cement binders, facilitated by microfracturing, resulting in the breakdown of CSH compounds to calcite in the presence of atmospheric CO_2.

Within modern times (the last 100-150 years or so) since industrial portland cements became available, evaluation of concrete durability during this period has shown that the CSH compounds have not exhibited any form of degradation, although hydration of the cement is incomplete *[Mallinson and Davies, 1987]*. For example, samples of 60 year old portland cement were taken from hydroelectric power tunnels in Porjus, Sweden. Cores were drilled from the concrete walls of the tunnels and the cement pore water was pressed from the matrix *[Allard, et al., 1984]*. The resulting crushed material was used in radionuclide sorption experiments run in parallel with modern concrete samples. The Porjus concrete and pore water were found to be remarkably fresh. One possible explanation is that carbonation formed a protective skin on the concrete mass reducing leaching and other interactions with the flowing water in the tunnel. Analogue studies have also encompassed the identification of naturally-occurring CSH compounds in a number of lime-rich geological formations *[Milodowski et al., 1989]*. Most of the identified minerals (up to 40 in number) tend to be very rare and are restricted to specific temperature/pressure boundary conditions which do not conform to predicted repository conditions. Even so, they have remained stable within these hydrothermal environments for periods amounting to tens of millions of years, provided they are protected from present-day weathering. Otherwise, as noted for the archaeological examples, the CSH compounds rapidly alter to calcite.

Clay in contact with concrete is of importance for repository performance. Clay may be used as backfill around underground concrete constructions (SFR) or together with concrete walls forming impermeable tunnel seals. In reality it may also be difficult to avoid using concrete in underground tunnel construction, e.g. for stabilising fracture zones by injection etc., prior to backfilling and sealing tunnels and deposition holes with clay. Concrete pore water will also have an influence on the bentonite clay constituents and vice versa. For example, potassium, calcium and hydroxide ions from concrete pore water with a high pH will transform clay minerals such as sodium montmorillonite which is the important swelling component of bentonite. On the other hand, carbonate and sulphate ions from bentonite will react with components of Portland Cement and presumably change its porosity and structure. Old construction concretes embedded in clay have been studied but little change has been noted *[Andersson and Fontain, 1981]*.

Natural analogue studies which can be directly applicable to a low- to intermediate-level cementitious repository are presently being conducted in the Maqarin region of N.W. Jordan *[Khoury et al., 1992; Alexander et al., 1992]*. The chemistry of source rock is defined by the spontaneous combustion of bitumen-rich marls, followed by low temperature hydration of the high temperature mineral assemblage, eventually forming cement minerals such as portlandite, ettringite and thaumasite. Thus, in addition to the high pH groundwater environment (by interaction of normal groundwaters with the cement minerals), the likely sequence of source leachates (NaOH and KOH followed by $Ca(OH)_2$) is precisely that predicted by various models of cement degradation in groundwater.

8.2.3 Bitumen

In the Swedish low- to intermediate-level waste programme, up to 25% bitumen will be used as a matrix material to solidify the wastes. Both geological and archaeological occurrences of bitumen have been used as analogues to ascertain its stability and preservation properties in varying geochemical environments. This is based on the premise that technological bitumens (i.e. the distilled fraction of petroleum) are physically and chemically comparable to natural bitumens (maturation of natural organic matter in sediments) used, for example, in ancient times. Recent reviews of natural analogues to bitumen have been given by *[Hellmuth, 1989a]* and *[Miller, 1992]*. However, as pointed out by *[McKinley and Alexander, 1992]*, very little information is available for relevant high pH conditions.

Qualitatively , the geological occurrences of natural bitumens (e.g. asphalt lakes; bituminous marl formations; Oklo uranium deposit associations etc.) point to their stability under a wide range of physico-chemical conditions. Climatically, they are found in tropical to permafrost, arid to water-saturated conditions. These occurrences have been well documented but, unfortunately, little information exists regarding composition, degradation/aging and weathering processes. A few detailed studies have been reported, e.g. *[Hellmuth, 1989b]*; however, the observed degradation of bitumen (mainly to humic and fulvic acids) has occurred slowly under superficial, oxidising conditions (enhanced by visible and ultraviolet light), which do not reflect the repository environment. Furthermore, the alteration kinetics are very slow at low temperatures below 100°C, which conforms with the temperatures expected in a repository. In addition, Hellmuth (1989a) underlines the potential danger of microbial decomposition of hydrocarbons, which may be a problem prior to, and immediately after, closure of the repository.

Long-term, radioactive waste isolation properties of bitumen under assumed reducing conditions is presently being studied at Oklo *[Nagy et al., 1991]*. Initial results suggest that the Oklo reactor uraninites, which incorporated fission products during criticality, where held immobile within resolidified graphitic bitumen until geologic events some 1 Ga following criticality resulted in some mobilisation of U and Pb. Even so, the uraninite encased in solid graphitic matter in the organic-rich reactor zones lost virtually no fissiogenic lanthanide isotopes during this later event.

Short-term preservation properties of bitumen can be observed from archaeological artifacts; even in Babylonian times (1300 B.C.) it had been long used to preserve organic material (e.g.

wooden boats, roofing, baskets etc.). In almost all cases were artifacts have been found coated in bitumen, they have been well preserved except when mechanical damage to the bitumen has occurred, due to a hardening of the bitumen coatings with time. Of-course, many of these examples derive from oxidising conditions, but, if it is assumed that such conditions are more aggressive than predicted for a reducing repository environment, then it is reasonable to expect that the isolation and preservation properties of bitumen would remain stable in a repository situation.

In general, natural and archaeological analogues studies presently support the stability, preservation and immobilising properties of bitumen under the temperature and redox conditions predicted to prevail in a repository situation. However, the absence of high pH groundwater conditions associated with many of the examples documented is a point of concern. The project at Maqarin, Jordan, is presently trying to remedy this situation by studying the interaction of high pH groundwaters with a bituminous marl formation *[Alexander et al., 1992]*. The bitumen is rich in many trace elements, including uranium, considered important to repository safety assessments. Initial results indicate that whilst certain trace elements may be preferentially mobilised, the bituminous matrix is relatively resistant *[McKinley and Alexander, 1992]*.

9. Summary and conclusions

Despite their growing popularity over the years, the application of natural analogues and geological systems to the performance assessment of radioactive waste disposal has been mainly a supportive one. This may be attributed to the seeming lack of quantitative data produced which can obviously be used by the performance assessors, combined with a general misapplication of those data which have emerged. Recent advances have been made, however, mostly as a result of improved interaction between geoscientists, experimentalists and performance assessors. Field (and laboratory) programmes of study are now being better focussed towards the ultimate goal of providing useable data for performance assessment.

The main onus of natural analogue studies described in the literature has been to identify and quantify the natural occurrences of various geochemical processes expected to occur in and around a radioactive waste repository. Almost all studies relate to the engineered barrier system and geochemical mass transport of radionuclides and other trace elements in groundwaters. By broadening the scope of this report to include geological systems, the possibility now exists, for example, to include glaciation and neotectonics, as separate issues of direct influence on performance assessment.

An attempt has been made in this report to review a selection of the most important natural system studies carried out to date, outline the main analogue applications to performance assessment, provide a compilation of performance assessment applications already reported in the literature, present some new performance assessment related issues not previously described and suggest some general recommendations for further development in this field. This account is not meant to be an exhaustive analysis of existing data; there has not been the time or the resources to tackle all the issues as comprehensively as desired. It should therefore be seen as a step forward towards the integration of data from natural analogue studies as well as studies of natural geological systems into a repository performance assessment context.

9.1 Groundwater redox conditions

Groundwater redox conditions constitute an important input to many of the geochemical codes and databases used in the validation of performance assessment related trace element solubility and speciation modelling. It has always been difficult to measure redox conditions in groundwater because of the generally very low concentrations of redox active species. For example, iron(II) ions are usually present at the microgram per litre level. In reality the redox buffering capacity of the system depends more on the concentration of mafic minerals that supply, for example, the iron to the water. To improve on field measurements, it was found that the redox conditions could be characterised by the simple analysis of Fe(II), pH, HCO_3 and temperature in groundwater, in combination with field observations of the age and crystallinity of fracture filling iron minerals in contact with the groundwaters.

Sufficient data were not available from all of the considered sites, but there were enough to demonstrate that such an approach holds considerable promise as long as the groundwater redox system is buffered by the Fe(II)/Fe(III) redox couple. Swedish groundwaters were found to correspond to equilibrium conditions with aged Fe(III) precipitates, such as crystalline goethite, whilst at Poços de Caldas (and Alligator Rivers) the data indicated active precipitation of $Fe(OH)_3$; in all cases these Fe-oxyhydroxide phases were identified in the field. Cigar Lake calculations revealed two Fe-oxyhydroxide generations which correspond closely to field observations. In contrast, the Swiss site groundwaters, because of the presence of additional redox buffer couples, showed little agreement. The Finnish data also suggest that other redox couples may be active in the groundwaters.

Although not an analogue study in itself, this evaluation of groundwater redox potential is a good example of model development partly driven by the demands of natural analogue studies, i.e. the demand for a sound database and for reliable input values to test geochemical models. Moreover, the studies of natural analogues have provided a wealth of data on different geochemical systems and thus contributed to an increased confidence in our understanding of the systems that govern the groundwater redox conditions. This is essential for the credibility of the performance assessment.

In general, testing the redox model showed that:

- the model is validated for a wide range of deep groundwater conditions, especially variations in pH and alkalinity,

- as the model is reliable, it should therefore be possible to simplify quantifying groundwater redox conditions by omitting direct measurement of E_h, provided that the other parameters are accurately determined.

Furthermore, the uranium concentration in the groundwaters at the different sites is low, in accordance with the E_h as defined by the model.

Recommendations

For every analogue (and site-specific) area:

1. Accurate groundwater in situ measurements of Fe(II), pH, HCO_3 and temperature

2. Precise mineralogical identification of fracture Fe-oxide and Fe-hydroxide phases

3. Calculation of E_h

4. Comparison with other redox-active substances such as uranium, sulphur species, etc

9.2 Testing geochemical codes and databases

In recent years, some of the most valuable applications of natural analogues to performance assessment have been in testing the geochemical models (i.e. the geochemical codes and databases) used to calculate radionuclide solubility and speciation in groundwaters, and their sorption behaviour in contact with fracture mineral assemblages. Chemical thermodynamic models provide two main types of data for repository assessment purposes: a) solubilities of particular elements or radionuclides (this parameter places an important constraint on release rates from, e.g. spent fuel), and b) speciation of such elements in solution (allows their transport properties to be estimated).

To test such models, a series of "blind" solubility predictions have been carried out, notably at Oman, Poços de Caldas, Cigar Lake and Maqarin. In the Poços de Caldas study five different groups participated in the exercise, at Maqarin four groups while the Oman and Cigar Lake studies each involved one group. Selected major element analyses of groundwaters were used as input to predict the solubility, speciation and solubility-limiting solid phase for a number of elements considered important in repository performance assessment (e.g. U, Th, Pb, Ba, Cu, Sr, Mo, As, Sn, Se, Mn, Ni and Ra). The predictions were then compared with observed aqueous concentrations, speciation and trace mineralogy. From all sites there was reasonable agreement between the predicted solubilities and the measured trace element concentrations. Discrepancies occurred, however, in the predicted aqueous speciation. This was particularly obvious for uranium, indicating the large uncertainties which still exist in the solute speciation databases. To help tackle this problem, experimental field in situ speciation techniques were attempted at Poços de Caldas, but unfortunately with only limited success.

In most cases where calculated elemental equilibrium concentrations deviate from the measured concentrations the models results are higher than the measurements. There are several possible reasons for this. The models presume that the system is at thermodynamic equilibrium. This may not be the case as kinetic processes may be of importance. Moreover, the data bases used may not be complete, and, in particular, it may not contain the minerals actually limiting the solubility in the real system. It is likely that solid solutions and other mixed minerals that are not generally included in the data bases play a role in this context. In some cases, it can be suspected that a lack of mineral source for the trace element gives rise to a concentration below equilibrium.

It should be borne in mind that even though close agreement may be achieved between different groups modelling the same groundwaters, this does not necessarily indicate that the predictions are correct. The use of chemical speciation codes is entirely dependent on the quality of the input data; the more reliable the data the better the result. This uncertainty of the geological source terms and the corresponding doubt as to whether concentrations observed reflect trace element solubility limits or if release rates are insufficient to reach saturation concentrations, is a major limitation to this analogue approach.

The correct identification of the solubility controlling solid phase is very important, particularly with respect to influencing at an early stage the analytical requirements of ongoing analogue studies. For example, producing a list of predicted solid phases may help focus mineralogical studies. Thus, after several iterations of modelling and mineral identification, a more quantitative and realistic suite of solid phases can ultimately be produced.

Recommendations

1. Such "blind" predictive exercises should ideally involve the comparison of several codes and databases thus facilitating an integrated approach to identifying areas of uncertainty and/or lack of data within different thermodynamic databases.

2. More effort is required to develop reliable in situ speciation techniques.

3. Continued major effort to identify fracture mineral phases known to be in contact with the sampled groundwaters.

9.3 Radionuclide chemistry and transport in the near-field

The near-field formation and propagation of redox fronts resulting from oxidation processes (e.g. radiolysis), accompanied by radionuclide transport, was addressed using examples from Oklo, Cigar Lake and Poços de Caldas. Studies of radiolysis are exemplified at Oklo (mainly gamma) and Cigar Lake (both alpha and gamma) and redox front propagation at Poços de Caldas. However, caution should be exercised when comparing Cigar Lake, presently a low temperature groundwater environment more in line with the disposal concepts of SKB and TVO, to that at Oklo, which today represents a dry fossilised hydrothermal environment.

Studies show that radiolysis processes do occur in nature influencing the "near-field" redox chemistry which can result in localised oxidation and radionuclide mobility. Model calculations at Cigar Lake confirm that the radiolysis products of water oxidise Fe(II) to Fe(III) which may then precipitate due to low solubility. This might account for the characteristic red colouring due to the presence of trivalent iron (as Fe-oxyhydroxides) evident at the ore/clay boundary. However, it is uncertain as to whether all the Fe(III) minerals can be accounted for by this process. Within the orebody mineralogical evidence also points to some oxidative effects, i.e. the presence of higher mixed uranium oxides; furthermore hydrogen gas (known to result from radiolysis/water reactions) has been measured in the groundwater from the orebody.

Radiolysis evidence at Oklo is believed to have resulted in a net reduction of iron to its divalent form, probably accompanied by a net increase in total iron, associated with the reactor zone rocks; the aureole rocks showed less extreme reduction features. Furthermore, some of the fissionable products are believed to have undergone oxidation and subsequent migration away from the reactor zone.

Taken collectively, present results support the fact that radiolytic oxidation in the near-field of exposed spent nuclear fuel, within the concept of an underground repository, cannot be ruled out. However, studies at Cigar Lake indicate that the net changes are considerably overestimated by models currently used by performance assessment. The presence of some oxidation in the orebody indicates that the UO_2 in spent fuel will not necessarily consume all the oxidants generated.

The outward propagation of redox fronts from the radiolytic source at the canister/bentonite interface, and their migration rates, depends on the nature and geometry of the disposal concepts involved, and may involve distances from centimetres to hundreds of metres per Ma. Low temperature redox front migration is best exemplified in the Poços de Caldas study. Based on estimated geomorphological net erosion rates of the Poços de Caldas plateau, and assuming that the downward migration of the redox fronts was dependent on the rate of erosion, the average rate of redox front movement was calculated to be around 10 metres per Ma which is roughly comparable to the rates expected to occur around a repository.

As predicted by the near-field model, redox-sensitive radionuclides are also observed to precipitate as they pass in solution through the redox front. This is particularly convincing at Poços de Caldas (for uranium and its decay daughters) and also at Oklo (for several fission end products); however further detailed studies are needed at Cigar Lake to confirm similar processes. At Poços de Caldas it has been shown that reduction/precipitation mechanisms, as well as scavenging by coprecipitation and sorption, take place at the redox fronts. Some of the substances reduced (e.g. UO_2 and SO_4) are found in the order of centimetres downstream of the front. It has been postulated that the reduction of these species may be kinetically controlled.

The models used, however, cannot be considered predictive as they greatly simplify the system being described.

Some of the elements enriched at the Poços de Caldas redox fronts (e.g. Cs) are not recognised as sensitive to redox conditions and as such are not expected to be precipitated as a result of solubility limitations. The enrichment of these elements are therefore likely to be caused by sorption or coprecipitation with, for example, ferric iron hydroxides. This may very well have important performance assessment implications as there exists the potential for interaction between easily soluble radionuclides and canister corrosion products.

Processes relating to coprecipitation or solid solution of radionuclides in Fe-oxyhydroxides cannot presently be simulated by current near-field models. Their role has not been quantitatively included in performance assessment models due to a lack of appropriate data. Neglecting this phenomena may be conservative, but then again this might lead to an overestimation of concentrations by many orders of magnitude. The observed magnitude of this phenomenon was unexpected before the investigations, thus serving to identify an important feature that had been overlooked in early performance assessments. This is a good example of how natural analogue studies can help to recognise processes which are non-linear and therefore unpredictable in a precise and deterministic fashion.

Observations at both the Cigar Lake and Oklo sites, further supported by coupled mass transport calculations at Cigar Lake, endorse the efficiency of the clay halo as a barrier to radionuclide and trace element migration. At Cigar Lake, the massive clay (metres) surrounding the ore effectively shields the orebody hydrologically and also acts as a buffer to geochemical reactions and release processes. At Oklo, although the clay-rich alteration rim around the reactor is contrastingly very narrow (centimetres), its retardation properties at hydrothermal temperatures have been impressive. These studies therefore strongly support the integrity of the bentonite overpack intended for waste disposal, despite the fact that illite, rather than the more stable smectite considered in disposal concepts, characterises both the Cigar Lake and Oklo sites.

Recommendations

1. Further development of models to more accurately predict field observations. In particular:
   - net changes expected to occur from radiolysis
   - reduction/precipitation at the redox front

2. The minor UO_2 oxidation observed in the Cigar Lake orebody, in contrast to the predicted extent, may suggest that oxidative/reductive radiolytic reactions are occurring and the that UO_2 is effectively being reconstituted in situ resulting in the matrix release of some of the trace elements while the UO_2-matrix remains essentially intact. More work is recommended in this area and Cigar Lake appears to be the best site.

3. The hydrothermal nature of the Oklo reactors makes them less applicable to the SKB and TVO disposal concepts. However, assuming that radionuclide mobilisation and diffusion processes etc. will be more active at higher temperatures than at the lower temperatures expected from the SKB and TVO disposal concepts, then further quantification of the mechanisms which characterise these fossil reactors (i.e. worst case scenario) is recommended.

9.4 Radionuclide chemistry and transport in the far-field

Central to any repository performance assessment is an estimation of the mass transport rate of radionuclides from the near-field engineered overpack out into the geosphere and ultimately to the biosphere. As a general rule, mass transport models applied to data from natural analogue studies try to simulate the current spatial distribution of some natural tracer from its source. The use of uranium (and its decay daughters) as a source term has many advantages: a) it constitutes a natural groundwater tracer, b) it conveniently occurs as concentrations in rock at depths and in hydrogeological environments comparable to many disposal concepts, and c) it is the major component of spent nuclear fuel, i.e. a direct chemical analogy.

The study of far-field processes in the context of natural analogue studies have mainly been restricted to the large-scale, multiprocess analogue sites, such as Poços de Caldas, Alligator Rivers and Cigar Lake. Of special importance is an understanding of the present (and past) hydrogeological groundwater flow environment of the sites and, specifically, the nature of groundwater interaction with the radioactive source term, i.e. usually a uranium orebody. Ideally, groundwater transport paths to and from the orebody should be confined and rock and groundwater sampling points restricted to these paths.

Radionuclide mass transport

Movement and retardation of radionuclides through the geosphere has been dealt with under the general headings of transport (advection/dispersion), channelling, colloidal influence and retardation mechanisms such as matrix diffusion. Standard radionuclide models (commonly applied to performance assessments) and more complex coupled chemical transport models have been applied to simulate field observations.

Transport models of the type commonly used in repository performance assessment have been used to simulate radionuclide migration in the shallow weathered zone of the Koongarra uranium deposit in the Alligator Rivers region. Some important factors, however, were neglected, for example, weathering of minerals and hydrological variations due to seasonal climatic fluctuations. Nevertheless, a simple model, using the observed migration distance, estimates of the groundwater velocity, estimates of sorption equilibria (K_d) measured in the laboratory, and measured isotopic disequilibria between ^{238}U, ^{234}U and ^{230}Th in whole rock samples, indicated that uranium migration had occurred over a period of 1-3 Ma. By including hydrodynamic dispersion in the model, setting the migration time to 2 Ma, assuming that the groundwater flux and K_d are constant with time, and using different input value ranges, the results generally confirmed a uranium migration time of 1-2 Ma and the shape of the concentration front was better simulated using a dispersion length of 1 m rather than 10 m.

A more complex model considered both seasonal climatic fluctuations and weathering processes. The weathered zone was treated as two, one-dimensional transport pipes, geologically different, with seasonal fluctuation represented by connecting pathways. Weathering effects assume that the rock consists of an accessible phase to the water flow (uranium phase in sorption equilibrium with uranium in groundwater) and an inaccessible phase. Uranium transfer occurs between these phases by α-recoil. Preliminary results support the experimental K_d values and groundwater flux estimates and found that the exchange rate of uranium between accessible and inaccessible phases was of the order of the decay constant for ^{234}U and that the migration time is less than 2 Ma.

These different modelling attempts give a fairly consistent picture of uranium migration in the weathered zone, in the order of 1 Ma. However, palaeohydrogeological studies are still necessary to accommodate climatic variations which are known to have influenced this region within the last million years.

In the Cigar Lake study, due to an initial lack of suitable performance assessment mass transport models that could be directly applied, a series of three iterative models were subsequently developed to describe the system. In contrast to Alligator Rivers, where uranium mobilisation and transportation have been measured, the Cigar Lake site shows very little field evidence of uranium mobilisation and migration. All the models were therefore based on the assumption that uranium was being mobilised from the orebody. Two of the models, one involving molecular diffusion and advection with a rapid transfer of uranium without interaction/retardation effects, and the other coupling uranium migration with possible geochemical processes, showed that uranium movement did not extend beyond the massive clay halo surrounding the deposit.

A further model, however, considered the mass transport of in situ nuclear capture products (^{36}Cl, ^{14}C and ^{3}H) from the ore through the clay to the porous altered sandstone; enhancements of both ^{14}C and ^{3}H have been measured in groundwaters from the altered sandstone close to the deposit. Transport processes were considered to be by diffusion (through the clay) and advection (within the sandstones). The results showed that the released plume of nuclear products through the clay halo (most of the products are contained by the clay) would tend to be restricted to the bottom of a very narrow downstream layer, and that concentrations would be very low. These findings essentially supported the field observations and the conceptual hydrogeological model for the Cigar Lake deposit.

Recommendations

1. Other analogue sites are required for study, particularly in fractured crystalline rock more in common with Fennoscandian conditions.

2. Radionuclide transport paths need to be more restricted to specific conductive fracture zones intersecting a uranium orebody. This would facilitate integrated rock and groundwater sampling and eventual mass transport modelling as the boundary conditions would be more constrained and better defined.

Channelling

The flow of groundwater through a fractured crystalline rock via a network of anastomosing channels has long been accepted by the geoscientific fraternity. Recently the performance assessment implications for far-field transport (i.e. rapid transport pathways) and retardation mechanisms (i.e. less fracture surface area available) have been recognised and attempts have subsequently been made to quantify this phenomenon. However, field evidence is rare and the evidence is difficult to quantify.

Two contrasting field examples can be mentioned; one supporting channelling, the other not. For the first example, an attempt was made to quantify channelling at the Osamu Utsumi uranium mine, Poços de Caldas, where the infiltration pathways of downward migrating oxygenated groundwaters through fractures in the bedrock (by channelling?) could be traced. This was possible by measuring the extent of oxidised rock which had become altered through contact with these waters prior to them becoming reducing. These pathways could be mapped from mine exposures and by interpretation of exploration geochemical distribution maps produced for each different excavation level. Uncertainties in the modelling included the absence of site-specific data on the distribution of channels and the groundwater flow-rates in the channels. To compensate for this, observational data (such as channel frequency) from the Swedish SFR low- to intermediate-waste facility were extrapolated. The frequency of channels in the Swedish bedrock was in the order of 1/20 m^2 to 1/100 m^2, whilst at the Osamu Utsumi mine frequencies in the order of 1/1000 m^2 were indicated. This discrepancy is partly due to the impossibility of reconstructing channel distributions in the excavated rock at the different mine levels, and due to the exclusion of fine channels because of the coarse resolution used in the mapping.

Although of limited value, this study helped to underline the importance of certain parameters such as the distribution of flow-rate and the interconnecting pattern network of the channels.

The second example, where channelling is less convincing, involves hydraulic interference pump testing, rather than visual observations. The area is Finnsjön in central Sweden where a considerable amount of study was devoted to a low-angle sub-horizontal fracture zone. The conclusions reached after detailed hydraulic and hydrochemical investigations were that measurements at several locations within the same zone indicated a rapid and uniform response to both hydraulic and tracer tests over distances of up to 400 m. This uniformity of character would strongly argue against channelling in this particular case; it is highly unlikely that the same system of channels could be intercepted over such a large area. The zone quite simply is open and highly permeable over its areal extent. Consequently, and with respect to performance assessment, the apparent absence of channelling within this fracture zone at Finnsjön may very well give rise to fast flow coupled with increasing dilution with the overall effect of a decrease in radionuclide retardation. The study also showed the unimportance of channel interconnections traversing the sub-horizontal zone; the zone forms a very efficient hydraulic and hydrochemical barrier to water flow from surface to depth.

One further mention could be made from the Stripa studies of Zone H *[Olsson (Editor), 1992]*. In common with Finnsjön, but on a much smaller scale, four out of six boreholes drilled within an area of approx. 2 m^2 showed hydraulic connection and uniform hydraulic conductivity. Once again, this would tend to argue against channelling in this instance.

Particularly in the Stripa case it could be argued that the hydraulic gradient situation deviates from the natural, and that this could severely influence the paths that are available to the flow and transport. In other words, increased gradients that are directed selectively to a sampling point of measurement (sampling of tracer or pressure response measurements). In addition, blasting, drilling and decompression of the rock may have opened up new paths. The fact that hydraulic testing indicates a connectivity does therefore not necessarily constitute evidence that connected flow paths would exist under natural gradients in an undisturbed rock.

To conclude, the character, distribution and dynamics of channelling in crystalline rocks is still not well known with confidence. More studies are needed before a quantitative appraisal can be conducted. Natural analogues could potentially provide data on tracers that have moved under undisturbed conditions for long periods of time.

Recommendations

1. Additional observations of natural oxidation patterns from mine exposures and quarries may prove useful.

2. More use should be made of chemical tracers to map potential channel pathways along fracture planes. The excavation of tunnels etc. could facilitate the choice of suitable tracer injection locations along recharging fracture zones. Injection could be from the bedrock surface down into the tunnel, or, from the floor of the tunnel to greater depths, or both. In each case large-scale excavation of block material could be carried out after suitable injection times. Such experiments are presently being planned at the Äspö Hard Rock Laboratory in Sweden.

Matrix diffusion

Matrix diffusion is potentially a very effective retardation process to far-field radionuclide transport and, if verified, has important implications on performance assessment. The major implications are that sorbing radionuclides are not just limited to the fracture surfaces, but by diffusing through the fracture coatings they have access to a much greater rock matrix volume.

Natural analogue studies are probably more reliable than laboratory data in most respects by virtue of realistic time-scales and that the measured radionuclide profiles represent processes which have been occurring under natural groundwater and overburden pressure conditions. A considerable amount of laboratory and field data have now been compiled and reviewed. Natural analogue studies, mainly focussing on diffusion penetration depths, have been conducted in a variety of hydrogeological environments and some kind of pattern seems to be emerging. Most penetration depths range from 1 mm up to 50 mm (values of 50 cm have also been mentioned); the higher range values are most commonly observed in fractures which have undergone alteration (usually early hydrothermal) and the lower range values from relatively "fresh" fractures.

Unfortunately few field data exist at the moment for deriving diffusivity coefficients; this is often due to practical considerations such as sample size restrictions etc. which inhibit the fine measurement of physical parameters. Moreover, considering those data available, a confusingly large range of values for granites have been reported (10^{-19} to 10^{-10} m^2/s). At the moment, therefore, emphasis must still be put on laboratory-derived values; it should be pointed out that such data should be treated with caution (as experimental artifacts tend to produce overestimations) and should be considered as non-conservative.

Direct application of matrix diffusion data to performance assessment has been made in the Swedish KBS-3 analysis *[SKB, 1983]*, which assumed that the diffusion could extend through the granite matrix, and later in the Swiss Gewähr analysis *[Nagra, 1985]*, which assumed a maximum penetration depth of 1 mm. More recently, in the Swedish SKB-91 *[SKB, 1992]* performance assessment an apparent diffusivity of $1.9 \bullet 10^{-17}$ m^2/s was chosen for uranium in granite. This value, derived from laboratory data, was compared with calculated diffusion depths as a function of time for different values of apparent diffusivity. Comparison using this simple diffusion model showed that natural analogue observations corresponded to diffusivities of the order of 10^{-18} to 10^{-16} m^2/s. This was interpreted as lending credence to the input value chosen for the SKB-91 study.

In general the basic theory of matrix diffusion has been clearly verified from natural analogue studies, at least for fractured crystalline rocks, with connected porosities extending well into the rock matrix. Furthermore, the combination of observed penetration depths of uranium and estimated time-scales are in good agreement with predictions with a simple diffusion model using apparent diffusivities based on laboratory measurements. However, more quantitative field studies are required to support this statement.

Recommendations

1. More radionuclide profile measurements are required and, in general, should be supported by detailed petrographic and geochemical studies, measured physical rock parameters (e.g. porosity, diffusivity, permeability etc.) and groundwater chemistry at the location of the profiles. Physical parameters have tended to be neglected, usually because of the sample size restrictions of the drillcore material. Large-scale specimens should be selected from underground excavations.

2. In particular, more fracture radionuclide profile measurements are required from "unaltered" water-conducting zones.

3. Many of the reported measured profile data derive from randomly selected samples. Rock profiles should be systematically selected representing oxidising through to reducing bedrock and groundwater conditions.

The role of colloids

A major interest in performance assessment is the potential far-field transport of trace elements distributed between groundwater, the fracture surfaces and the colloid or particulate content in the groundwater. To date no model exists to quantitatively accommodate these processes. The role of colloids is usually regarded as unimportant, colloids being considered immobile, produced and present in too small concentrations, and that interaction with elements is restricted to rapid and reversible sorption mechanisms. In principle, colloids can cause dissolution of radionuclides above their solubility limits and prevent sorption on rock mineral surfaces. If this occurs to any notable extent, then the colloids would act as a "short circuit" to the important barriers of solubility and sorption.

One of the major problems of studying colloids is the difficulty of sampling and extracting the colloidal material from groundwaters. For example, excessive pump extraction rates (leading to particle dislodgement and groundwater mixing) and/or residual drilling debris can lead to overestimation of the particle contents. Even though considerable effort has been devoted to improving sampling methodology, uncertainties remain and there is still much room for improvement, particularly in fractured rock media.

Colloids have been studied from several of the analogue sites; Alligator Rivers, Poços de Caldas, Cigar Lake, Broubster etc. In most cases the separated colloid size fractions have been chemically analysed (major and trace element ions, uranium decay series and REEs) and physically classified (size, shape, mineralogical character etc.). In general, the total colloid concentrations were found to be quite low, for example at Morro do Ferro they were < 1 mg/L, and that colloid transport of radionuclides was found to be relatively unimportant. Uranium migrates mostly as dissolved species, whereas thorium (+ actinium and REEs) is mostly associated with larger, relatively immobile particles (> 1.0 μm) such as amorphous Fe-oxyhydroxides and clays which reflect the local fracture mineralogy. There is some evidence from Broubster that fulvic acid can contribute to keep hexavalent uranium in solution thereby promoting transport. At Morro do Ferro the uptake of three- and tetravalent elements by the colloidal particles was stronger than anticipated.

The natural analogue observations generally support the assumption that colloidal transport of uranium and REEs is of little significance in the performance assessment. The reasons for this could be either that sorption of uranium, thorium and lanthanides onto naturally occurring colloids in the groundwater is reversible, or that the colloidal particles are immobile. It is likely, from the observations, that the colloids are efficiently filtered by the geological medium at the studied sites (e.g. Morro do Ferro and Broubster). There is no major evidence of massive transport of colloid-bound radionuclides or other trace elements. However, an important observation at the Krunkelbach mine in Germany drew attention to clay colloidal material characterised by increased Mg and Ti signatures, when compared to the surrounding granitic media. The only source for these chemical anomalies was a gneiss formation some 1-2 km distant. The important inference made was that these colloids had been transported over such distances within fractured crystalline rock.

Unfortunately, the application of analogue-derived data to performance assessment is very sparse due to the complexities of sampling, separation and sensitivity to groundwater chemistry (e.g. mixing). This is exemplified in the recent SKB-91 analysis *[SKB, 1992]* which was based on laboratory-derived input data rather than analogue studies. In this assessment a very simplistic approach was taken assuming that radionuclides emanating from a breached canister are irreversibly sorbed on the colloids which were transported unhindered along the groundwater flow path to the biosphere. Laboratory-based sorption coefficients were used for elements such as Cs, Sr, Ni, lanthanides and actinides. For some of these elements, measurements were made on generated colloidal material comprising typical granitic-type particles of silica, Fe-oxyhydroxides and clays. For other elements, crushed granitic rock material was used. The calculations indicated that even if irreversible sorption is assumed, there would be no dose consequences at the biosphere interface. It was pointed out, however, that due to the complexities of natural systems, this analysis may not be as robust as desired.

Recommendations

1. Further attempts should be made to improve sampling and separation of colloidal material at realistic extraction rates based on quantitative hydraulic information

2. Discharge, artesian conditions should be preferred

3. Downhole in situ measuring techniques should be encouraged

4. Additional analogue studies are needed, particularly in fractured crystalline rock similar to Fennoscandian conditions.

9.5 The role of microbes

It is an established fact that microbes have been identified in deep Swedish groundwaters down to 1 km depth, and that they play an important role in the evolution of groundwater chemistry (e.g. by influencing iron oxidation and sulphate reduction), although their efficiency very much depends on the supply of nutrients and the absence of extreme conditions such as high temperature, high pH, radiation effects etc. The repercussion of microbial activity on repository performance assessment (both high- and low-level wastes) centres around gas generation, canister corrosion, redox reactions, formation of complexing agents and radionuclide groundwater transport.

Gas generation

Gas generation, mostly methane, carbon dioxide and hydrogen, results from the breakdown of cellulose and other organic waste materials (CO_2 and CH_4) and the canisters (H_2) particularly if composed of steel. In many cases gas generation is either a direct result of, or mediated by microbial activity.

Performance assessment of the Swedish SFR intermediate-level repository *[SKB, 1987]* used, as an analogy, the anaerobic microbial production of methane and carbon dioxide from peat bogs and river bottom sediments which had been contaminated by cellulose from nearby paper and pulp mills. A gas production of less than 1 m^3 NTP per metric tonne of cellulosic waste per annum was predicted. Biodegradation of bitumen, leading to the production of carbon dioxide and enhanced steel corrosion, was also addressed in the SFR study. Analogies with laboratory studies and underground oil storage bunkers confirmed microbial degradation of bitumen-related hydrocarbons.

Natural analogue applications to bitumen behaviour are difficult to find. Reference to Maqarin and Oklo have been made, but both suffer from the disadvantage that hydrocarbons other than bitumen are present. The term "bitumen" is too loosely defined when natural hydrocarbon occurrences are described. Some qualitative information has nevertheless proved useful; for example, hydrocarbons at Oklo have survived for millions of years and appear to play a "protective" role to uraninite stability and fission product mobility, and at Maqarin hydrocarbon stability is suggested under high pH groundwater conditions, although fossil high pH reactions in similar rocks from Central Jordan contain no significant hydrocarbons. More quantitative data are required, particularly the identification and classification of hydrocarbon types.

Corrosion

The presence of aqueous sulphide is a potential threat to the integrity of the metal materials (mostly steel and copper) used in repository construction. Bacterial influences (mainly sulphate-reducing forms) on canister corrosion have recently received widespread attention in connection with low- to high-level radioactive waste repositories. As an example, sulphate-reducing bacteria have been associated with the corrosion of steel oil-well casings. It is generally expected that aerobic corrosion will dominate until air trapped in the sealed repository has been consumed, whereupon anaerobic corrosion will take over. Limiting factors to microbial activity are the availability of nutrients and energy; specifically for sulphide-reducing bacteria, the major limiting factor is the supply of electron donors from sources such as organic material and hydrogen and methane gas.

With regard to pitting corrosion, analogous occurrences exist in nature of microbial activity which serve to illustrate the localised nature of these phenomena. For example, reduction spheres (cm to dm in size and often containing sulphide ore phases) occur in an otherwise oxidised and hematite-rich host rock. It has been conjectured that these spheres may have resulted from sulphide-reducing bacteria, although an external source of reductants would also have been necessary. Of particular concern to disposal concepts therefore, is the localised nature of the activity (i.e. pitting), the production of sulphides and the unknown external source of reductants. A further evaluation of this analogue is recommended to further elucidate the consequences of sulphate reduction. On the brighter side, trace elements, including uranium, are retained within the spheres and, moreover, the spheres take a long time to develop.

Microbial activity and oxic corrosion of canister and reinforcement materials (from residual trapped oxygen) have also been addressed in performance assessments. Pitting, observed in domestic copper water pipes, has been attributed to microbial activity; furthermore, this has been reproduced under laboratory conditions. Contrastingly, no major microbial activity has been associated with the well preserved Swedish bronze canon from the 17th century warship, Kronan. Even though residing in brackish waters, albeit partially submerged in clay sediments, the rate of corrosion was estimated to be less than a cm during a 100 000 year period. However, microbial activity may explain the reduction of surface tenorite (CuO) corrosion products to copper sulphides.

Redox reactions

Bacterial reactions, in addition to mediating metal corrosive effects, also serve to lower the solubility of some radionuclide elements by decreasing the redox potential and generating sulphide; in the absence of bacteria, sulphate reduction would not occur at ambient temperatures. Bacteria may also play an important role in catalysing reactions such as the oxidation of Fe(II) and sulphide minerals and the reduction of U(VI). For example, oxidation of iron and pyrite contained in bentonite results in a reduced system prohibiting further oxidation. However, these reactions may not require the presence of microbes. This is preferable from a performance assessment viewpoint as it increases reliability, predictability and therefore confidence in repository behaviour. Reliance on bacterial action would, at best, be dubious.

Some evidence can be gleaned from the Poços de Caldas redox front analogue studies which shows that microbial activity is not always necessary for pyrite oxidation. In this study the oxidation of pyrite was shown to be remarkably fast when compared with diffusion. Moreover, sulphur-oxidising bacteria were not found at the redox front. This is not proof, but a rather strong indication that pyrite oxidation at the redox front will proceed as a series of pure inorganic reactions when similar circumstances are maintained.

Reduction of dissolved U(VI) at a redox front is another interesting reaction from the performance assessment point of view. This reaction is predicted to be sluggish and, as shown by the Poços de Caldas studies, U(IV) is not precipitated immediately but a few centimetres ahead of the redox front on the reducing side. Uranium is precipitated as pitchblende nodules, often together with secondary pyrite. The role of microbes in these reactions was also investigated at Poços de Caldas but no clear answer was found.

Complexing agents

Bacteria are known to generate organic acids that form strong complexes with many metal ions; this results in a general lowering of solubility limits and sorption coefficients. This phenomenon has been considered in performance assessments carried out for low- to intermediate-level waste disposal. For high-level wastes, however, no such bacteria-derived organic agents are considered; small amounts of humic and fulvic acids, naturally present in deep groundwaters, are assumed to lower the sorption coefficients somewhat, but are not expected to influence the solubility to any significant extent. The presence of bacteria, in this context, is of concern if strong complexing agents are produced. This would effectively increase the solubility, mobility and dispersion of many important radionuclides thus rendering the near-field barrier system less efficient.

The potential influence of bacterial action on, for example, trace element solubility, can be tested by evaluating some of the solubility and speciation exercises which have been an integral part of the some of the natural analogue studies. These studies essentially show that by calculating trace element concentrations in groundwaters, assuming only inorganic speciation, and comparing the result to the measured concentrations, no significant influence of organic complex-forming substances (whether bacterially mediated or otherwise) have been found in deep groundwaters. At this present stage in analogue studies, the repercussions of bacterial action on deep, high-level repositories would not appear to be significant.

It should be pointed out, however, that this work is still at its infancy; reliable microbial sampling techniques from deep groundwater sources and associated rocks still need to be improved. This is not only necessary to characterise the "natural" microbial content of deep groundwaters, but knowing this will also provide a reference microbial "population" to assess the amount and type of contamination expected to occur during repository construction and sealing.

Radionuclide transport

In groundwater microbes can both retain dissolved radionuclides (when attached to the fracture mineral faces) and transport them (when suspended in groundwater). These two possibilities were addressed in the SKB-91 performance assessment analysis; it was demonstrated that microbes do not have the capacity to significantly influence radionuclide migration. This, however, was based on average microbial contents of deep groundwaters related to laboratory experiments on the uptake of sorbing radionuclides on relevant bacteria.

In nature such microbial processes are much more complex and, as still, not largely understood. Even though, some attempt has been made to use the absence of colloid transport of radionuclides at sites which also have abundant organic material available (e.g. Morro do Ferro and Broubster). As these conditions are conducive for bacterial activity, the absence of any colloidal transport therefore indicates that the influence of microbes on radionuclide migration must also be negligible.

Recommendations.

1. More natural geological systems need to be studied of radionuclide dispersion analogues in general, and colloid transport analogues in particular.

2. It is important to improve the sampling and characterisation of bacteria under "representative" groundwater conditions.

3. More studies of microbial influence on typical repository construction materials and waste forms under various hydrogeochemical (and laboratory) conditions would be very useful.

4. Further laboratory studies of the complexation and sorption of radionuclides in the presence of different bacteria types.

9.6 The effects of glaciation

The onset of future glacial conditions, coinciding with the projected life-span of a permanent repository for high-level radioactive waste, is cause for some concern regarding the long-term assessment of repository performance. It is quite clear that cyclic glacial periods have occurred within recent geological time, and will very probably continue to occur, at least within the initial important 100 000 a, and most likely throughout the estimated time of high-level spent fuel containment, i.e. one Ma. It is therefore important to put the life-span of the repository into a glacial perspective.

The possible effects of a glaciation on the integrity and safety of a repository can be studied through observations of present-day glacial conditions and evidence from past glaciation periods. Although not strictly a natural analogue in the classic geochemical sense, glaciation is here viewed as a potential perturbation of a technological system through disruption of the natural geological host environment, and as such can thereby influence the long-term performance of a repository.

Studies of Quaternary deposits and landforms, present ice masses and a quantitative understanding of periodic changes of the earth's orbit around the sun, have provided sufficient data to predict with reasonable certainty that major changes in glacial/stadial conditions will occur at approx. 60 000 a, similar in magnitude to the last glacial maximum with a duration of 20 000 - 25 000 a. There is also general support for a 20 000 a glaciation; one occurring after approx. 5 000 a is less certain. The TVO/SKB ice scenario bases its concept on the assumption that smaller or larger glaciations will occur at approx. 5 000, 20 000 and 60 000 a, and that interglacial conditions (i.e. similar to present-day conditions) will not become established until approx. 75 000 a. At the earliest, man will not resettle in Fennoscandia until after approx. 5 000 a, assuming that a glaciation will occur at this time.

Glacial and interglacial periods will undoubtedly put the bedrock under variable stress, and it is the ability of the bedrock to accommodate such stress that provides the crux to repository safety. Present evidence supports current repository conceptual models which consider that any crustal movement will be "buffered" by readjustment within and along preexisting bounding fracture zones (i.e. "deformation barriers"), rather than affecting the rock block mass which houses the repository.

Changes in hydraulic conductivity and groundwater chemistry would appear to pose the greatest threat to repository safety, although these affects should be mainly confined to existing hydraulic pathways in the far-field, i.e. the same structural features which bound the repository mechanically. There are two major concerns about the chemical stability of the near-field engineered barriers: a) the incursion of oxidising, low ionic strength groundwaters, and b) the incursion of saline groundwaters.

It is conceivable that highly oxidising, alkaline melt waters of low ionic strength and low carbonate content could reach repository depths. The penetration of such waters over long periods of time might serve to diminish the overall redox buffering capacity of the bedrock and reduce the efficiency of the bentonite overpack thereby increasing potential radionuclide mobility. However, it is well to point out that no dramatic present-day subsurface changes in bedrock chemistry can be directly related to the last deglaciation, at least not to any marked depth.

Glaciations can potentially influence the accumulation of saline water in the repository, for example, by introducing marine water, by remobilising deep saline groundwater and by fractionation due to freezing during permafrost formation. The existence of these mechanisms for saline water intrusion is supported by observations in nature. Saline water can have a detrimental effect on the properties of the near-field barriers. For example, the bentonite is influenced by the salinity which alters properties such as swelling pressure and pH. Moreover, with regard to canister stability, saline water contact could alter the existing thermodynamic boundary conditions for canister corrosion (e.g. if there was an appreciable increase in chloride together with a low pH) such that reactions involving only oxygen and sulphide would no longer be applicable, . However, most saline groundwaters studied seem to be characterised by high pH (7-8), rather than values of 4 and less required for corrosion.

It has been speculated that gas derived from within the rock mass may become frozen as clathrates (gas hydrates) within the permafrost zone or trapped beneath as a gaseous "cushion". Thawing may result in an explosive release of the contained gases. At the moment these geogas effects are not considered to be a major problem because of the small volumes of dissolved gas presently detected in groundwater.

However, at our present state of knowledge radioactive leakage during glaciation is not considered a major problem. Few if any people will inhabit these regions and strong dilution of any leaking waste products will minimise any doses thereof.

Recommendations

The major recommendation is the further study of existing continental ice sheets (Greenland and Antarctica) and particularly their influence on the subsurface hydrogeology and hydrogeochemistry. Some inroads are presently being made through deep drilling programmes.

9.7 Construction materials

9.7.1 High-level waste

The near-field barriers are an important part of the repository system, and to analyse their performance constitutes a central part of the overall performance assessment. The near-field is usually thought of as comprising the engineered barriers that are in contact with, or located in the immediate vicinity of, the waste. The safety-related functions of the engineered barriers are to contain the radionuclides in the waste during the initial disposal period so that comparatively short-lived radionuclides decay, and also to help limiting the release rates of the radionuclides from the waste once the containment (the canister) has been penetrated. This is achieved by placing the waste in a canister of sufficient durability and by surrounding it by a buffer material that protects the canister both from mechanical forces (e.g. due to rock movements) and from flowing groundwater. The engineered barrier system consists of the matrix of the waste form (UO_2 in the case of spent fuel or borosilicate glass in the case of HLW from reprocessing), a canister containing the waste form, a clay buffer surrounding the canister and the backfill in tunnels and shafts which consists of a mixture of clay and sand.

The materials comprising the engineered barrier system have important physical properties, the suitability of which must be demonstrated over the very long time-scales (hundreds to thousands of years) required to assess the safety performance of a repository. Various models are used to extrapolate the laboratory characterisation of barrier behaviour. However, to validate these models, which relate to short-term material degradation over hundreds to thousands of years, is beyond conventional engineering experience. Validation, even though being only partial, is therefore sought by the natural analogue approach.

Waste Form

The features of the waste form which are of interest in performance assessment essentially relate to the variability of the physico-chemical properties of the waste with time, i.e. chemical, thermal, mechanical and radioactive properties. Chemical alteration of the matrix will lead to the release of radionuclides; this may occur by the dissolution of the UO_2-matrix or by oxidation of UO_2 to form higher uranium oxides with contrasting crystalline structures. Elements bedded in the original matrix can thus become released and come in contact with the aqueous phase. Mechanical fracturing of the waste can increase the surface area available for alteration, and radioactive effects can lead to radiation-induced dissolution transformation to other solid phases by corrosion reactions.

Spent nuclear fuel is the preferred waste form for both the SKB and TVO high-level radioactive waste programmes. The major waste component in spent fuel is UO_2 ($>95\%$), together with matrix impurities such as nuclear fission products, actinides and actinide daughters. Laboratory studies on the stability of spent nuclear fuel, critical for understanding the initial, or short-term corrosion behaviour during temporary storage and initial permanent disposal, are well documented. Mechanisms of spent fuel alteration have essentially been identified through laboratory experiments conducted on pure UO_2, real spent fuel and simulated spent fuel. However, predicting the behaviour of fuel over thousands of years falls outside the scope of experimental extrapolation.

Laboratory experiments on spent fuel stability show that dissolution is slow to minimal under any conditions which approach those expected in and around a repository. Furthermore, laboratory studies show that UO_2 dissolution is sometimes accompanied by the formation of solid uranyl phases on the fuel surface.

Naturally occurring uraninite or, the less pure variety of pitchblende, are commonly considered analogous to spent fuel, containing in some cases up to 90% UO_2, but important dissimilarities do occur. There are also important differences in morphology between UO_2 minerals and spent fuel. Despite these differences, however, the study of natural uraninite ore and its surroundings provides important clues to the predicted long-term behaviour of spent fuel in a repository environment.

Natural analogues have been used to address the stability of uraninite/pitchblende under normal geological and repository conditions. For example, in northern Sweden it was shown that even though uranium mineralised fractures in crystalline rock (50-130 m depth) had been subject to water-rock interaction processes, the non-oxidative groundwater environment had preserved the integrity of the uraninite for most, if not all, of its 1.75 Ga existence, including the last 0.5 Ma when it has been closest to the earth's surface. Furthermore, the Cigar Lake analogue study indicates that at repository depths there is no convincing textural or chemical evidence of significant ambient low temperature removal of uranium under reducing groundwater conditions from the massive uraninite-dominated ore body since its formation some 1.3 Ga ago. As long as conditions remain reducing, the element is practically immobile; measured concentrations in groundwater are around 1 ppb, similar to UO_2 solubilities measured in the laboratory.

In the context of spent fuel stability, much attention has been given to the Oklo natural reactors which underwent criticality some 2.0 Ga ago resulting in the concentration of nuclear fission products, actinides and actinide daughters associated intimately with uraninite which crystallised from pitchblende during fission. The general stability of the uraninite since criticality to the present time has been demonstrated. However, important differences do exist when the uraninite is compared to spent fuel: a) uraninite contains lower concentrations of fission products, b) maximum temperatures reached in a reactor far exceed those experienced by the uraninite at Oklo; i.e. less fractionation in uraninite, and c) uraninite is better preserved than spent fuel because of a less complete nuclear reaction, thus rendering the reaction products less susceptible to mobilisation.

In uranium deposits which have not achieved criticality, nuclear reactions have, never-the-less, occurred in nature producing trace amounts of ^{99}Tc and ^{239}Pu in association with high-grade uranium deposits. For example, ^{99}Tc and ^{239}Pu have been studied from the Koongarra uranium deposit, Alligator Rivers, and ^{239}Pu has been measured from the Osamu Utsumi uranium mine, Poços de Caldas. These studies have shown that at Koongarra the uranium minerals have effectively retained ^{99}Tc and ^{239}Pu on a time scale of 1 Ma, and at the Osamu Utsumi mine ^{239}Pu has been retained on a time scale of at least 10^5 a; both results are reassuring for repository assessment considerations.

One potential problem, presently undergoing study at Cigar Lake, is the effect of oxidative/reductive radiolytic reactions on the natural uraninite crystalline structure which may have become reconstituted. This would effectively result in the matrix release of included trace elements and radionuclides, thus casting serious dispersions on the stability of spent nuclear fuel and in turn on repository performance assessment. However, such a mechanism is not reflected by the Oklo studies where radiolysis has also occurred, although, speculatively, this may be due to the "insulation" properties of the hydrocarbon materials which commonly enclose the uraninites within the reactor zones.

Recommendations

1. Detailed mineral chemical and physical studies of uraninite phases in varying redox environments, preferably from individual deposits, e.g. along mineralised water conducting fractures extending from oxidising to reducing groundwater conditions. This should allow the more sensitive oxidation changes to be more easily compared and contrasted and matrix release evidence more easily determined.

2. The effects of radiolysis on uraninite stability is still unclear; more studies of Cigar Lake and other nearby deposits is recommended; reconstituted uraninite (from stable isotopic evidence) has been found in association with more surface-related deposits in the Athabasca Basin.

Canister

The function of the canister is to isolate the spent fuel from groundwater contact for designated time periods ranging from thousands to hundreds of thousands of years depending on waste composition (reprocessing waste or spent fuel) and design goal. Copper, because of its thermodynamic stability in neutral to mildly reducing repository groundwater conditions, is the strongest candidate in the SKB and TVO programmes to encapsulate the spent nuclear fuel. Recently a more structurally stable alternative comprising a copper canister with an inner carbon steel support has been advocated; this is presently under review.

Generally, the life span of the copper canister depends on metal purity and the quality of the engineering (e.g. canister sealing), together with the composition of the groundwater (e.g. sulphide content) which it will ultimately come in contact with. Corrosion rates (0.025-1.3 μm/a) calculated from both historical and archaeological copper artifacts found in a wide range of wet/dry and oxic/anoxic environments demonstrates the long-term durability of copper, consistent with thermodynamic considerations. However, owing to the predicted low supply of oxidants expected to reach the canister (because of reducing repository conditions), only local corrosion attack (i.e. "pitting") is considered important. Safety assessment calculations for the KBS-3 concept involved a pitting factor of 5 (as observed from archaeological materials, e.g. the Kronan cannon) and an unfavourable case of 25 (as observed from the exposure of copper in soil). All available evidence from natural occurrences and archaeological artifacts showed that a pitting factor of 5 was more realistic, concluding that the proposed copper canisters should exceed their designed lifetime of 10^5 a by at least one order of magnitude.

One of the best natural analogues of copper is the existence (i.e. preservation) of massive native copper deposits of Precambrian age (around 500 Ma) on the Keweenaw Peninsula, Michigan, USA. The native metal has a very low impurity content (99.998 wt.% Cu); copper boulders, deposited during glacial melting 8 000 a ago, and therefore having been subject to large climatic extremes, exhibit only thin surface oxide coatings. By comparing abraded faces (resulting from glaciation) with unabraded faces (pre-glaciation surfaces), it has been calculated that time scales exceeding 1 Ma would be necessary to oxidise a 10 cm thick copper canister under such extreme conditions.

Contrastingly, natural analogues for steel (e.g. NAGRA disposal concept), which is a relatively recent technological alloy, are mostly limited to geological or archaeological artifacts. Iron meteorites and archaeological artifacts comprising iron or iron alloys have been categorised, native iron occurrences have been studied at Disko Island, Greenland, and archaeological artifacts such as a horde of Roman iron nails discovered at Inchtuthil, Scotland, are described. Although no useful analogue information on localised corrosion (i.e. pitting) of iron or steel is available, the most appropriate data indicate a total corrosion time for a NAGRA-type container to be anything from 10 000 to 250 000 a.

In summary, there would appear to be adequate archaeological and geological analogue evidence to support the stability of copper over the large time-scales necessary for reliable performance assessment predictions, but is it enough? More examples to support the steel canister concept is desirable. It is recommended that the quest for geological and archaeological metal analogues should continue to locate examples (such as the Kronan canon) within specific hydrogeological and hydrogeochemical environments where the boundary conditions can be more precisely defined.

Recommendations

1. Archaeological artifacts of copper and iron in, for example, domestic water wells/springs which have been in use during long periods of historical time should be further investigated. In such a case it may be possible to date the artefact and also quantify the groundwater environment which may not have changed significantly during the ages.

2. Archaeological and geological metal artifacts in brackish to saline, reducing to oxidising, groundwater environments has a potential to provide useful information.

Bentonite Buffer

The function of the buffer material is to: a) constitute a mechanical and chemical zone of protection around the canister, b) limit the inward transport of potentially corrosive substances from the groundwater to the canister surface, c) in the event of canister corrosion, to limit the dispersion of leached radionuclides from the canister out into the bedrock, and d) filter fine particulate and colloidal material that may form during leaching of the waste.

One of the major problems regarding the use of bentonite is the conversion of smectite clay (which includes Na-bentonite) to illite clay during increases in temperature, pressure and water circulation. Analogue studies of bentonite stability have therefore involved long-term naturally occurring scenarios of clay alteration in different geological and thermal environments. For example, bentonite stability under laboratory conditions, within the range of 100-130°C (i.e. the maximum temperature range expected to result from thermal loading during spent fuel disposal), is not well established. Natural analogue studies of naturally occurring bentonite showed that even having experienced temperatures of 110-120°C over a period of 10 Ma, there was no evidence of any adverse effects on the buffer properties. At higher contact metamorphic temperatures (105-240°C) the results indicated that even though there was substantial illitisation at temperatures up to 110°C (maintained for several hundreds of years), there was no obvious loss in plasticity or expansion properties on hydration. These analogue observations thus play an important role when stating that the thermal pulse predicted in the deposition hole will not result in any deterioration of the clay barrier.

Anaerobic corrosion of steel components in high-level waste (e.g. canisters) and low-level waste (e.g. reinforcement) can generate gas in the form of hydrogen *[Werme, 1990]*. Other gas-forming processes such as microbial degradation of organic materials etc have to be anticipated for certain low-level wastes. If the gas is generated at such a high rate that it cannot escape by diffusion a separate gas phase will be formed. The diffusivity of dissolved hydrogen in bentonite is relatively low. Therefore, if clay is used as a buffer around, for example, iron canisters, it is necessary to estimate how generated gas can escape the system either by diffusion or by flow as a separate gas phase. The creation of a gas void will also displace water out of the system. Gas diffusivities as well as water and gas permeabilities are measured in the laboratory. Possibly there exist examples of these processes in nature.

A possible disadvantage with bentonite is its load-bearing capacity, i.e. the possibility of the canister sinking with time, reducing the bentonite insulation thickness between the canister bottom and the underlying bedrock. A further problem is the generally low thermal conductivity in contrast with the surrounding bedrock; even the bentonite/sand backfill material has higher thermal conductivity. Both of these aspects have not yet been fully addressed by suitable analogue studies.

In the context of hydraulic and elemental retardation properties, it is worth mentioning observations from the Cigar Lake uranium deposit and the Oklo uranium reactor occurrence, both of which are surrounded by an envelope of clay, mostly illite in composition. These clay layers have demonstrated their effectiveness, both as a hydraulic barrier against water circulation (Cigar Lake and possibly also Oklo) and a barrier to fission product migration (Oklo). Other examples of hydraulic integrity include the clay preserved tree forest at Dunarobba, Italy.

In summary, analogue studies of bentonite-type clays, representing a wide range of physical and chemical properties, show a consistent picture of alteration rates below those assumed for the safety analysis. At ambient repository temperatures (less than 80°C), they indeed suggest that the final maximum alteration will be well below 30%, and hence the assumption in the safety analysis that the bentonite properties will remain constant for at least 1 Ma, seems to be well justified.

Recommendations

1. Pursue studies relating to the load-bearing capacity of the bentonite; for example, search for natural occurrences of bentonite which incorporate large boulder occurrences. Exotic possibilities of Fe-meteorites embedded in bentonite-type materials.

2. Continued search for examples of geochemical influence on smectite-rich clay such as precipitation (silica, iron hydroxides, etc), redox reactions (oxidation of sulphides and iron(II) in clay), variations in pH (see also cement analogues), salinity, etc.

3. Continued search for suitable analogues to address the low thermal conductivity problem of bentonite. For example, small-scale dyke intrusions of high iron content. This may provide information combining thermal stability in the clays with subsequent insulation or otherwise from groundwater alteration of the dyke mafic mineral phases.

4. Gas and water permeability is of importance for the safety analysis. Clay analogues which have been subject to gas or water transport by diffusion or flow would be particularly valuable if such examples could be identified and quantified.

9.7.2 Low- to Intermediate-level Radioactive Waste

These wastes are packaged in steel drums and in concrete or steel containers. In some of these wastes, for example, ion exchange resins from the primary circuits, are solidified in a cement or bitumen matrix. Following final sealing and saturation of the repository, the near-field groundwater chemistry is predicted to become very alkaline and reducing. In this environment, the stability of concrete/steel constructions, the durability of the cement and bitumen matrices solidifying the wastes, and the nature of the breakdown products that may possibly enhance the solubility and subsequent transport of radionuclides, are therefore critical factors to the performance safety assessment of such repositories.

Concretes and Cements

The long-term integrity of repository construction materials such as cement, steel and bitumen in a highly alkaline groundwater environment is largely surmised only from laboratory-based modelled simulations. In the short-term, two analogue approaches have been used to study the durability of concretes and cements: a) archaeological building materials (hundreds to thousands of years), and b) industrial building material (tens to hundreds of years). The major problem with the archaeological material analogy is that modern concretes are composed of portland cement (mainly calcium silicates with little free lime) with chemical and physical properties much more extensive than ancient lime-based cements. However, some of the ancient cements also contain CSH (Calcium Silicate Hydrate) compounds, formed due to specific conditions of the cement preparation, which are the main hydration products of modern-day portland cement. These CSH compounds have consequently served to stabilise and preserve these ancient cements for up to 2000 years. It follows that with to-day's technology, CSH compound-bearing concretes should exhibit a durability even better than indicated from archaeological materials.

The stability of cement binders has been demonstrated by studies from Hadrian's Wall in northern England and from the Gallo-Roman baths in southwestern France. These studies confirm that the long-term carbonation of hydrosilicates is the dominant alteration mechanism of the cement binders. Furthermore, in more modern times (the last 100-150 years or so), industrial portland cements have shown that the CSH compounds have not exhibited any form of degradation, although hydration of the cement is incomplete.

Analogue studies have also encompassed the identification of naturally-occurring CSH compounds in a number of lime-rich geological formations. These tend to be very rare and are restricted to specific temperature/pressure boundary conditions which do not conform to predicted repository conditions. Even so, they have remained stable in various investigated hydrothermal environments for periods amounting to tens of millions of years, provided they are protected from present-day weathering. Otherwise, as noted for the archaeological examples, the CSH compounds rapidly alter to calcite.

Clay (used as backfill material) in contact with concrete is of importance for repository performance. Concrete pore water is expected to have an influence on the bentonite clay constituents and vice versa. Potassium, calcium and hydroxide ions (high pH concrete porewater) from the concrete will transform clay minerals such as sodium montmorillonite. Carbonate and sulphate ions from clay will react with cement (e.g. Ordinary Portland Cement) and influence its porosity and structure. In this respect old construction concretes embedded in clay have been studied but little change has been noted.

Natural analogue studies which can be directly applicable to a low- to intermediate-level cementitious repository are presently being conducted in the Maqarin region of N.W. Jordan. The chemistry of the source rock is defined by the spontaneous combustion of hydrocarbon-rich marls, followed by low temperature hydration of the high temperature mineral assemblage, eventually forming cement minerals such as portlandite, ettringite and thaumasite. Thus, in addition to the high pH groundwater environment (by interaction of normal groundwaters with the cement minerals), the likely sequence of source leachates (NaOH and KOH followed by $Ca(OH)_2$) is precisely that predicted by various models of cement degradation in groundwater.

The main disadvantage of the Maqarin site is that so far only the reactions occurring under oxidising groundwater conditions have been studied.

Recommendations

It would seem that most of the relevant information on concrete and cement has been gleaned from archaeological materials. What remains is the chance of finding a combination of materials (e.g. repository-related metal objects, cellulose, bitumen, clay minerals, etc.) in association with old degrading cements under reducing groundwater conditions, which may help to illuminate the range of interplay between different reactions.

The study at Maqarin would appear to be the most promising natural analogue study presently underway, and as much effort as possible should be made to further understand the processes occurring there. If the opportunity should arise, investigations should be expanded to include the reducing groundwater environment for comparison.

Bitumen

In the Swedish and Finnish low- to intermediate-level waste programmes bitumen will be used as a matrix material to solidify the wastes. Both geological and archaeological occurrences of bitumen and bitumen-related hydrocarbons have been used as analogues to ascertain its stability and preservation properties in varying geochemical environments. However, very little information is available for relevant high pH conditions.

Qualitatively, the geological occurrences of natural hydrocarbons (e.g. asphalt lakes; bituminous marl formations; Oklo uranium deposit associations etc.) point to their stability under a wide range of physico-chemical conditions. Unfortunately, little information exists regarding composition, degradation/aging and weathering processes. Of the observations recorded, the degradation of hydrocarbons (mainly to humic and fulvic acids) has occurred slowly under superficial, oxidising conditions, which do not reflect the repository environment. In addition, the alteration kinetics are very slow at low temperatures below 100°C, which conforms with the temperatures expected in a repository. Furthermore, the potential danger of microbial decomposition of hydrocarbons, which may be a problem prior to, and immediately after, closure of the repository, should again be stressed.

Long-term, radioactive waste isolation properties of bitumen-related hydrocarbons under assumed reducing conditions is presently being studied at Oklo. Initial results suggest that the Oklo reactor uraninites, which incorporated fission products during criticality, where held immobile within resolidified hydrocarbons until geologic events at 1 Ga following criticality resulted in some mobilisation of U and Pb. Even so, the uraninite encased in solid graphitic matter in the organic-rich reactor zones lost virtually no fissiogenic lanthanide isotopes during this later event.

Short-term preservation properties of bitumen can be observed from archaeological artifacts; even in Babylonian times (1300 B.C.) it had been long used to preserve organic material (e.g. wooden boats, roofing, baskets etc.). In almost all cases were artifacts have been found coated in bitumen, they have been well preserved except when mechanical damage to the bitumen has occurred, due to a hardening of the bitumen coatings with time. Of-course, many of these examples derive from oxidising conditions, but, if it is assumed that such conditions are more aggressive than predicted for a reducing repository environment, then it is reasonable to expect that the isolation and preservation properties of bitumen would remain stable in a repository situation.

In general, natural and archaeological analogues studies presently support the stability, preservation and immobilising properties of bitumen and related hydrocarbons under the temperature and redox conditions predicted to prevail in a repository situation. However, the absence of high pH groundwater conditions associated with many of the examples documented is a point of concern. The project at Maqarin, Jordan, is presently trying to remedy this situation by studying the interaction of high pH groundwaters with a Bituminous Marl Formation. The hydrocarbons are rich in many trace elements, including uranium, considered important to repository safety assessments. Initial results indicate that whilst certain trace elements may be preferentially mobilised, the hydrocarbon matrix is relatively resistant. However fossil reactions, similar to those presently occurring at Maqarin, and some hundreds of thousands years old, exist in Central Jordan. The disturbing fact is that no hydrocarbon material apparently remains; more studies are required in this region.

The major disadvantages in the study of natural analogues to understand the behaviour of bitumen are: a) the general absence of bitumen; many of the hydrocarbons studied are a form of kerogen, b) the absence of interacting high pH solutions (exception of Maqarin), and c) little information exists on the bitumen stability in the presence of saline water.

Recommendations

1. Continuation of the Maqarin analogue project specifically to:
   - compare high pH reactions under reducing groundwater conditions
   - detailed analysis of the much older fossil high pH reactions preserved in Central Jordan

2. The search for other areas with bitumen/high alkaline reactions should continue

3. Asphalt blocks originating from great depths along the Dead Sea Rift Valley have been reported floating in the Dead Sea. These, and other reported occurrences of asphalt in the same area at varying depths, would seem an ideal opportunity to study hydrocarbon-saline water interactions.

Acknowledgement

The authors would like to thank Juhani Vira (TVO) and Lars B Nilsson (SKB) for their reviews which have greatly improved this report. Constructive suggestions from Ian McKinley (Nagra) and Russel Alexander (RWIG Berne) on an earlier version of the report are avknowledged.

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Stress redistribution and void growth in buttwelded canisters for spent nuclear fuel

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TR 93-02

Hydrothermal field test with French candidate clay embedding steel heater in the Stripa mine

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TR 93-03

MX 80 clay exposed to high temperatures and gamma radiation

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December 1992

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Project on Alternative Systems Study (PASS)

Final report

October 1992